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THE
PHYSICAL REVIEW

NOTE ON THE STATISTICS OF NUCLEI

By P. Ehrenfest and J. R. Oppenheimer
California Institute of Technology, Pasadena

(Received December 23, 1930)

Abstract

From Pauli's exclusion principle we derive the rule for the symmetry of the wave functions in the coordinates of the center of gravity of two similar stable clusters of electrons and protons, and justify the assumption that the clusters satisfy the Einstein-Bose or Fermi-Dirac statistics according to whether the number of particles in each cluster is even or odd. The rule is shown to become invalid only when the interaction between the clusters is large enough to disturb their internal motion.

I. Introduction

THE band spectra of symmetric diatomic molecules show certain striking differences from those of asymmetric molecules. For when the two nuclei of the molecule are identical, the intensity of the individual lines of a band, instead of varying smoothly from line to line, alternates more or less markedly. This alternation may in most cases be understood[1] with the help of a simple rule, but in the case of the N_2 molecule, the theoretical prediction seems to disagree with experiment, in that it leads us to expect those band-lines to be the more intense, which are in fact weaker. In this paper we do not propose to resolve this disagreement; we shall only try to give as direct a derivation as possible of the rule which plays the cardinal part in obtaining the theoretical prediction. For it seems that, in spite of the frequent citations of this rule, no explicit derivation of it from Pauli's exclusion principle has been published. In giving this derivation we shall have to investigate the conditions under which the rule is valid, and the degree of approximation to which it may be expected to hold.

The rule may be stated:

R. "If we have two nuclei, each built up of n electrons and m protons, and if the nuclei are in the "same inner state," then not all the molecular states which would be possible for an asymmetric molecule will be found to occur; if $n+m$ is $\begin{cases}\text{even,}\\ \text{odd,}\end{cases}$ only those states $\begin{cases}S\\ A\end{cases}$ will occur for which the wave function $\begin{cases}\text{remains unchanged}\\ \text{changes its sign}\end{cases}$ when we interchange the "coordinates" of the nuclei.

[1] See the comprehensive report by R. S. Mullikan, Transactions of the Faraday Society **25**, 611 (1929).

When the nuclei are in different states, the molecule behaves like an asymmetric molecule."

Since we may expect the nuclei to be in their normal state, we should be able by this rule to predict the weight of the states S and the weight of the states A if we knew the degree of degeneracy g of the normal states of the nuclei. Thus there will always be $\frac{1}{2}g(g-1)$ states S and $\frac{1}{2}g(g-1)$ states A possible; if n plus m is even, there will be g states S, if n plus m is odd, g states A, also possible. The relative weights of the states S and A will therefore be

$$\begin{aligned}&(g+1)/(g-1) \text{ if } n+m \text{ is even}\\&(g-1)/(g+1) \text{ if } n+m \text{ is odd.}\end{aligned} \tag{1}$$

If we ascribe the degeneracy of the normal state of the nuclei to the spatial degeneracy of an angular momentum $sh/2\pi$, then these ratios become

$$\begin{aligned}&(s+1)/s \text{ for } n+m \text{ even}\\&s/(s+1) \text{ for } n+m \text{ odd.}\end{aligned}$$

From this we see that, since $n+m$ is odd for the nitrogen nucleus, the states A should have a greater weight than the states S. According to the assertions of band spectroscopists, the electronic wave functions of the normal state of the N_2 molecule are symmetric in the coordinates of the nuclei, and there is no resultant electronic angular momentum parallel to the molecular axis. If we accept these assertions, we are led to expect a greater weight for states of odd rotational quantum number than for those of even quantum number; and it is this expectation which is not confirmed by experiment.

Our problem is now so to refine the expressions "internal state" and "interchange the coordinates of the nuclei" in our rule R, that we can derive the rule from the exclusion principle.

II. Wave Packets for a System of Two Clusters

We shall consider first the following preliminary problem: Suppose that we have a system containing $2n$ electrons and $2m$ protons. Suppose further that for any group of n electrons and m protons we could write down a complete set of wave functions u_k for the stationary states k; how then, using any two of these wave functions u_k and u_l, can we build up a wave packet for the whole system which satisfies the exclusion principle for all the electrons and all the protons in the system? Only when the particles of the system do not interact at all will these wave packets represent the stationary states of the whole system; but with the help of these packets, by linear combination, we shall be able to build up wave functions which do represent stationary states for any interaction energy of the particles. The functions u may for instance represent states of a nucleus, or an atom, or a molecule, or even some aperiodic motion of the n plus m particles; for this preliminary problem we need to make no assumption about them; but we shall see later that only when the functions u represent very stable configurations: i.e. very tight binding of the particles,—can we deduce any significant results; and so we shall call any group of n electrons and m electrons a cluster.

Let the cartesian coordinates, referred to a fixed axis system, and the component of spin in a fixed direction, of the jth electron be x_j; similarly let the coordinates and spin of the ith proton be y_i. Let us split up each of the functions u into two functions, a function T_s which depends only on the coordinates of the center of gravity of the cluster, and a function ψ_σ which depends on the relative coordinates of the particles, and on the spin variables:

$$u_k(x_1 \cdots x_n, y_1 \cdots y_m) \rightarrow T_s(x_1 \cdots x_n, y_1 \cdots y_m)\psi_\sigma(x_1 \cdots x_n, y_1 \cdots y_m) = T_s(\alpha)\psi_\sigma(\alpha)$$

$$u_l(x_{n+1} \cdots x_{2n}, y_{m+1} \cdots y_{2m}) \rightarrow T_t(x_{n+1} \cdots x_{2n}, y_{m+1} \cdots y_{2m})\psi_\tau(x_{n+1} \cdots x_{2n} y_{m+1} \cdots y_{2m}) = T_t(\beta)\psi_\tau(\beta)$$

We write α for the arguments $(x_1 x_2 \cdots x_n, y_1 y_2 \cdots y_m)$ and β for the arguments $(x_{n+1} x_{n+2} \cdots x_{2n}, y_{m+1} y_{m+2} \cdots y_{2m})$

Since T depends only on the sum of the coordinates of the electrons, and the sum of the coordinates of the protons, and does not involve the spins at all, it must remain unchanged when we make an arbitrary permutation of the arguments x of u among themselves or of the arguments y of u among themselves. On the other hand u must be antisymmetric in its arguments x and in its arguments y, since otherwise it could not represent a stationary state for the cluster allowed by the exclusion principle. Thus ψ must be antisymmetric in the x's and in the y's. Let now P be an operator which makes an arbitrary permutation of the x's and an arbitrary permutation of the y's in any function of $x_1 \cdots x_{2n}, y_1 \cdots y_{2n}$, and let p be the order of the permutation P. Then the functions

$$F_{st,\sigma\tau} = \frac{1}{(2n)!(2m)!} \sum (-)^p P \{ T_s(\alpha) T_t(\beta) \psi_\sigma(\alpha) \psi_\tau(\beta) \} \tag{2}$$

satisfy the exclusion principle, if the summation be taken over all the $(2n)!$ $(2m)!$ permutations P. There are only $r = (2m)!(2n)!/(m!)^2(n!)^2$ different terms in this sum, since by the antisymmetry of the ψ's, all of the terms in which the arguments of T_s (and therefore also of T_t) are the same have just the same value. If we define a distribution by the symbol $(x_j \cdots, y_i \cdots | x_f \cdots y_g \cdots)$ in which the arguments of T_s are to the left, those of T_t to the right, of the line, and in which the order of the arguments to the left and to the right is indifferent, then we can write

$$F_{st,\sigma\tau} = \frac{1}{r} \sum{}' (-)^p P \{ T_s(\alpha) T_t(\beta) \psi_\sigma(\alpha) \psi_\tau(\beta) \} \tag{3}$$

where now the summation is taken only over the r different distributions. Now in $F_{st,\sigma\sigma}$ with $\sigma = \tau$, we can combine the term with the distribution

$$(x_j \cdots y_i \cdots | x_f \cdots y_g) \tag{4}$$

with that with the inverted distribution

$$(x_f \cdots y_g \cdots | x_j \cdots y_i).$$

This second term may be derived from (4) by n plus m interchanges, and will therefore appear in the sum with the same sign as (4) if n plus m is even, and with the opposite sign if m plus n is odd. We may therefore write, with $\theta = (-1)^{m+n}$

$$F_{st,\sigma\sigma} = \frac{1}{r}\sum{}''(-)^{p}P\{\psi_\sigma(\alpha)\psi_\sigma(\beta)[T_s(\alpha)T_t(\beta) + \theta T_s(\beta)T_t(\alpha)]\} \tag{5}$$

where now the summation is taken over the $r/2$ different sets of arguments in the ψ_σ's. When $\tau \neq \sigma$, we have instead,

$$F_{st,\sigma\tau} = \frac{1}{r}\sum{}''(-)^{p}P\{\psi_\sigma(\alpha)\psi_\tau(\beta)T_s(\alpha)T_t(\beta) + \theta\psi_\sigma(\beta)\psi_\tau(\alpha)T_s(\beta)T_t(\alpha)\}$$

which we may write

$$\begin{aligned} F_{st,\sigma\tau} = \frac{1}{2r}\sum{}''(-)^{p}P\{ &[\psi_\sigma(a)\psi_\tau(\beta) + \psi_\sigma(\beta)\psi_\tau(\alpha)][T_s(\alpha)T_t(\beta) + \theta T_s(\beta)T_t(\alpha)] \\ &+ [\psi_\sigma(\alpha)\psi_\tau(\beta) - \psi_\sigma(\beta)\psi_\tau(\alpha)][T_s(\alpha)T_t(\beta) - \theta T_s(\beta)T_t(\alpha)]\} \end{aligned} \tag{6}$$

From (5) we see that $F_{st,\sigma\sigma}$ is $\begin{cases}\text{symmetric}\\ \text{antisymmetric}\end{cases}$ in s and t when $m+n$ is $\begin{cases}\text{even,}\\ \text{odd,}\end{cases}$ and, from (6), that for $\tau \neq \sigma$, $F_{st,\sigma\tau}$ has, for $n+m$ either even or odd, both a symmetric and an antisymmetric part, neither of which vanishes identically. These properties of the wave packets F will make it possible to deduce our rule.

III. Symmetry of Wave Functions for a System of Two Clusters

We should expect that these symmetry properties in s and t would persist in the stationary wave functions built up from the F's whenever the interaction of the two clusters was too small appreciably to distort the internal configuration of the clusters. In this paragraph we shall have to find the wave functions ϕ for the stationary states of the system of two clusters. We shall see that, when certain matrix components of the interaction energy of the particles may be neglected, the ϕ's do in fact have the same symmetry in s, t as the corresponding wave packets F; and we shall see further that the conditions under which we may neglect these matrix components are just those in which the interaction of the clusters does not greatly disturb their internal motion.

Let E be the energy of the system, and H the Hamiltonian; it will in general be given us as an operator on a function of the x's and the y's, and it will be 'impartial' to all x's and 'impartial' to all y's. The wave equation for $\phi(x_1 \cdots y_{2m})$ will be

$$(H - E)\phi = 0 \tag{7}$$

Since ϕ must satisfy the exclusion principle, and since our original u's formed a complete set of functions, we may expand ϕ as a linear function of the F's:

$$\phi = \sum_{\substack{(\sigma,\tau)\\ \sigma\neq\tau}} \sum_{s} \sum_{t} a(st, \sigma\tau)F_{st,\sigma\tau} + \sum_{\sigma} \sum_{(s,t)} a(st, \sigma\sigma)F_{st,\sigma\sigma}. \tag{8}$$

Here the summation $\sum_{\sigma\neq\tau}^{(\sigma,\tau)}$ is to be taken over all pairs (σ,τ) with $\sigma\neq\tau$, and $\sum_{(s,t)}$ over all pairs (s, t). We now introduce that part of the irreducible matrix for H which belongs to the term system satisfying the exclusion principle:

$$(st, \sigma\tau \mid H \mid s't', \sigma'\tau') = \int dV\, \tilde{F}_{st,\sigma\tau} H F_{s't',\sigma'\tau'}. \tag{9}$$

The integration $(\int dV \cdots)$ is to be taken over the whole domain of all the coordinates, and is to include a summation over the two values of all the spin variables. With the help of this matrix we may write the wave equation for the a's which is equivalent to (8):

$$\sum_{\substack{(\sigma,\tau)\\ \sigma\neq\tau}} \sum_{s} \sum_{t} (s't', \sigma'\tau' \mid H \mid st, \sigma\tau)a(st, \sigma\tau) + \sum_{\sigma} \sum_{(s,t)} (s't', \sigma'\tau' \mid H \mid st, \sigma\sigma)a(st, \sigma\sigma) = Ea(s't', \sigma'\tau'). \tag{10}$$

By (5), (6) we have

$$F_{st,\sigma\tau} = \theta F_{ts,\tau\sigma}$$

and

$$a(st, \sigma\tau) = \theta a(ts, \tau\sigma). \tag{11}$$

Suppose now that we may set

$$(st, \sigma\tau \mid H \mid s't', \sigma'\tau') = 0 \text{ for } (\sigma, \tau) \neq (\sigma', \tau'). \tag{12}$$

We shall have later to see under what circumstances, and to what approximation, (12) is legitimate; but if we accept it, then we see that (10) reduces to a series of independent equations, one for each pair of values of (σ, τ)

$$\sigma = \tau\colon \sum_{(s,t)} (\sigma\sigma, s't' \mid H \mid \sigma\sigma, st)a(\sigma\sigma, st) = Ea(\sigma\sigma, s't')$$

$$\sigma \neq \tau\colon \sum_{s} \sum_{t} (\sigma\tau, s't' \mid H \mid \sigma\tau, st)a(\sigma\tau, st) = Ea(\sigma\tau, s't')$$

For each such pair of values (σ, τ) we thus get a set of solutions $a\ (st)$; for $\sigma = \tau$ these will be $\begin{cases}\text{symmetric}\\ \text{antisymmetric}\end{cases}$ in s and t when $m+n$ is $\begin{cases}\text{even};\\ \text{odd};\end{cases}$ for $\sigma\neq\tau$ both symmetric and antisymmetric functions are possible. If we define the "state" of the cluster by the σ's, then this result is fully equivalent to the rule (R) given at the beginning of this paper. We may see this directly in the following way: for the quantum numbers s, t, we may take directly the value of the components of the total momenta of the two clusters; if we introduce the center of gravity coordinates of the two clusters, X, Y by the conditions

$$\begin{aligned} sX - Xs &= h/2\pi i; \quad sY - Ys = 0;\\ tY - Yt &= h/2\pi i; \quad tX - Xt = 0; \end{aligned} \tag{13}$$

then we get the transformation functions:

$$(st/XY) = e^{-2\pi i/h(sX+tY)}. \tag{14}$$

The wave functions for the stationary states of the whole system are then given as functions of X, Y by

$$\sum_{s,t} a(st, \sigma\tau)(st/XY). \tag{15}$$

For $\sigma = \tau$, these must be $\begin{cases}\text{symmetric} \\ \text{antisymmetric}\end{cases}$ in X and Y when $n+m$ is $\begin{cases}\text{even;} \\ \text{odd;}\end{cases}$ for $\sigma \neq \tau$ they may have either symmetry.

We have now only to consider the conditions for the validity of (12). If the states σ, τ of the isolated clusters are degenerate, then the matrix elements of H corresponding to transitions between such degenerate states—states in which the isolated clusters have the same internal energy,—may be made to vanish by choosing suitably the u's which give the stationary states of the clusters. The terms

$$(st, \sigma\tau \mid H \mid s't', \sigma'\tau')$$

in which the states (σ, τ) and (σ', τ') correspond to different energy levels of the clusters, will, since the original u's were chosen to make the internal energy of the isolated clusters a diagonal matrix, represent the matrix components of the interaction and interchange energy of the particles in one cluster with those in the other; and if the particles in the cluster are very tightly bound together, these energies will be very small compared to the energy differences of two stationary states σ, σ' of the isolated cluster. The terms which were neglected in (12) therefore, will give in this case only very small correction terms to the a's of the order of the ratio of the interaction energy of the two clusters to their proper energy; in general these correction terms will be neither symmetric nor antisymmetric in s and t, so that only for very stable clusters may we expect a rule like (R) to hold: for the two identical *atoms* of a symmetric molecule no such rule as (R) holds, since here the interaction energy of the atoms is of the same order of magnitude as their proper energy. Even in this case, of course, the exclusion principle for the electrons and protons reduces the number of possible stationary states; but here we cannot say just what states are excluded by investigating only the symmetry of the corresponding wave functions in the coordinates of the center of gravity of the clusters, but must study in detail the symmetry of the functions in the coordinates of all the elementary particles. The importance of the rule (R) arises from the circumstance, that in the dynamical treatment of most atomic and molecular problems we do not need to know anything about the structure of the nuclei, except that they are stable: we may treat them as point charges, with, in some cases, a spin s which gives a proper intrinsic degeneracy. And whenever this is so, we may use a rule like (R) to determine what states of the system survive the exclusion principle.

THE INTENSITY OF X-RAYS REFLECTED FROM PLATINUM, SILVER, AND GLASS

By Hiram W. Edwards
University of California at Los Angeles

(Received January 7, 1930)

Abstract

The intensity of a monochromatic beam of x-rays reflected from platinum, silver, and glass mirrors was measured for angles of incidence varying from 0.75 to 1.25 times the critical angle. Radiation having a wave-length of 0.69A was obtained by reflection from calcite. Values of the intensity of the reflected beam calculated by Thibaud's modification of Fresnel's equation were found to be in good agreement with experimental values obtained from platinum. Experimental results obtained from silver and glass mirrors do not agree quantitatively with the theoretical values. No explanation for the lack of concordance is offered.

LINNIK and Laschkarew[1] have observed that the intensity of x-rays ($\lambda = 1.537$A) totally reflected from an iron mirror does not fall off abruptly at the critical angle when increasing the glancing angle of incidence. Forster[2] attributed this lack of sharpness to an absorption effect in the reflecting medium. He attempted to derive an expression from the Fresnel reflection equations to express the intensity of the reflected x-ray beam in terms of the critical angles. Although Forster made an error in the derivation of his equation, the curves which he gave to show the effect of the absorption upon the intensity-glancing angle of incidence relation are in agreement with the curves, published later by Schon[3] and also with those given by Thibaud.[4]

Dershem[5] gave the relative intensities of the K_α line of carbon ($\lambda = 44.6$A) reflected from glass for angles of incidence varying from 1° to 8°. Thibaud[4] shows that Dershem's results are qualitatively in agreement with the values calculated by his (Thibaud's) extension of the Fresnel reflection equation.

The writer is not aware of any attempt having been made to check, quantitatively, the Fresnel equation of the intensity of reflected radiation in the x-ray region. In order to make a quantitative test three materials, platinum, silver, and glass, were selected. Platinum was chosen because of its relatively high absorption coefficient, silver and glass because of their low absorption coefficients. While the absorption coefficients of silver and glass are both low, the two materials are unlike in having relatively widely separated critical angles and are otherwise optically different.

[1] Linnik and Laschkarew, Zeits. f. Physik **38,** 659 (1926).
[2] Forster, Helv. phys. Acta **1,** 18 (1927).
[3] Schon, Zeits. f. Physik **58,** 165 (1929).
[4] Thibaud, Jour. d. Physique **7,** 37 (1930).
[5] Dershem, Phys. Rev. **34,** 1015 (1929).

Apparatus

The apparatus was arranged as shown in Fig. 1. The x-radiation was produced by a water cooled tungsten tube operated at 50,000 volts. The x-ray beam was defined by two slits, S_1 and S_2, each about 0.4 mm wide and about 80 cm apart. The x-ray beam was directed against a calcite crystal oriented so that a monochromatic beam ($\lambda = 0.69$A) was reflected. The tube voltage was sufficiently high to excite radiation up to a wave-length of 0.25A and consequently a second monochromatic beam of $\lambda = 0.345$A would be reflected from the calcite crystal along with the first. It is thought that the presence of the radiation of shorter wave-length did not appreciably alter the intensity measurements under consideration. If one assumes that the critical angles of the two radiations are proportional to the square of the wave-lengths, the critical angle of the shorter wave would be 0.25 of that of the longer wave, hence in the region investigated the intensity of the shorter wave must be very small as may be readily shown.

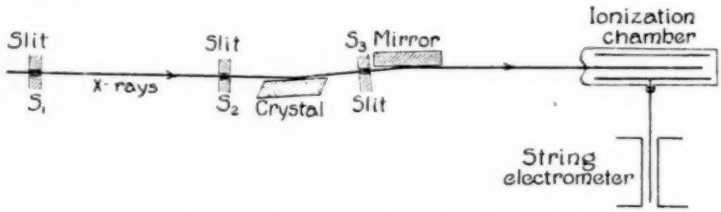

Fig. 1. Arrangement of apparatus.

The mirror under investigation was mounted on a spectrometer table and carefully placed parallel to the x-ray beam reflected from the calcite. The distance from the crystal to the mirror was approximately 27 cm. The axis of rotation of the spectrometer table was very nearly tangent to the surface of the mirror and approximately in the center of the incident beam. Both platinum and silver mirror were sputtered on pieces of glass (2×4.5 cm) which were flat within 0.5 of a wave-length of yellow light. The platinum mirror was opaque to visible light and thick enough to have a critical angle equal to that calculated by the Lorentz dispersion formula. The silver mirror would transmit about 5 percent of the visible light incident normally and not thick enough to give its maximum critical angle for this wave-length used. Three glass mirrors were used, all flat to within half a wave-length of yellow light.

It was found expedient to use a third slit S_3 in the optical system. This was placed very close to the mirror and served to limit the radiation to a very narrow beam the width of which was less than the length of the mirror multiplied by the smallest glancing angle of incidence used. By this arrangement all of the beam passing through the slit would strike the mirror surface and hence maintain an incident beam of constant intensity. At the same time the arrangement eliminated annoying scattered radiation which would have been present had any portion of the beam been permitted to pass by the mirror unreflected. Radiation scattered from the reflected beam caused no trouble.

The intensity of the reflected beam was measured by absorption in an ionization chamber and the rate of accumulation of charge on the string of a string electrometer. The sensitivity of the instrument was not determined but remained constant during any single series of observations. The front end of the ionization chamber was 65 cm from the center of the mirror.

The voltage across the x-ray tube was maintained constant within 1 percent. Filament current in the tube was practically constant.

The angle of incidence of the radiation upon the reflecting mirror was determined for a single position of the mirror by evaluating the particular reading of the tangent screw on the spectrometer table from measurements made photographically. For this purpose the slit S_3 was opened sufficiently to permit some of the radiations to pass by the mirror unreflected. The film was placed 63 cm from the mirror. Because of this comparatively short distance the angle could not be determined with an accuracy greater than about 3 percent.

Results

In the case of reflection of x-rays from metals or from glass it is necessary, because of the absorbing nature of the reflecting medium, to replace the ordinary index of refraction n, $(n = 1 - \delta)$, by the complex quantity n' where,

$$n' = (1 - \delta) - iK$$

and

$$K = \mu\lambda/4\pi$$

in which μ is the absorption coefficient and λ the wave-length.

Starting with the above expression and the Fresnel equation for the ratio R/I of the amplitude of the reflected wave, parallel to the plane of incidence, to that of the incident wave,

$$\frac{R}{I} = \frac{n \cos i - \cos i'}{n \cos i + \cos i'}$$

where i and i' are the angles of incidence and reflection measured from the normal to the surface, Thibaud[4] derived the following expression for the ratio (A) of the intensity of the reflected to that of the incident beam:

$$A = \frac{(1 + m)^2 + 2(m^2 + a^2)^{1/2} + 2(1 + m)(2(m^2 + a^2)^{1/2})^{1/2} \cos \phi/2}{(1 + m)^2 + 2(m^2 + a^2)^{1/2} - 2(1 + m)(2(m^2 + a)^{1/2})^{1/2} \cos \phi/2} \quad (1)$$

in which m is defined by the equation $\theta = (1+m)\theta_m$ where θ is the glancing angle of incidence, and θ_m is the critical angle. The other quantities are defined by the relations:

$$a = K/2\delta \quad \theta_m^2 = 2\delta \quad \tan \phi = -\frac{a(1 - \delta)}{m - a^2\delta}.$$

The following tables give the values of the constants used in calculating the intensities of the reflected rays.

TABLE I.

Mirror	μ	a	θ_m (radians)	$\delta \times 10^6$	$\lambda \times 10^8$
Platinum	2295.	0.078	0.00400	8.00	0.69
Silver	258.	.015	.00305	4.65	.69
Glass	17.4	.004	.00153	1.18	.69

The experimental and calculated values of the intensity of the x-rays reflected from the three materials are shown graphically in Fig. 2. Experimental observations are indicated by small circles and the calculated values are shown by small crosses.

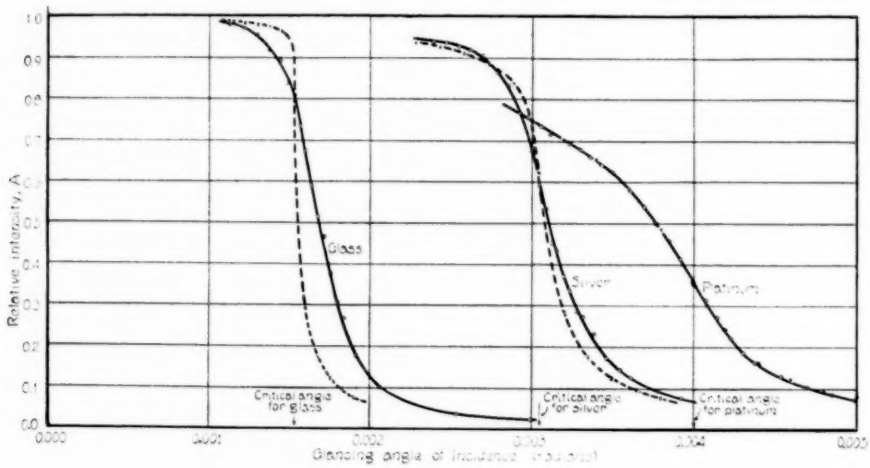

Fig. 2. Intensity of reflected x-rays.

The glancing angle of incidence is expressed in radians. Relative intensities are given in terms of the intensity of the incident beam taken at unity.

Because of the deviation of the calculated values from those obtained experimentally in the case of glass and silver, separate curves have been drawn to show the variation of intensity as determined experimentally and by computation.

Three different samples were used in obtaining reflection curves from glass and all yielded curves which were similar in form to that given in Fig. 2. The index of refraction was not the same in the three samples. The variation in δ was not large ($\delta = 1.18$ to 1.50×10^{-6}) and would have no appreciable effect upon the character of the intensity curve anyway. It was difficult to obtain a reliable value for the absorption coefficient because of the necessarily great thickness of the glass. Values of the absorption coefficient obtained from thinner pieces of glass which appeared to have the same composition did not differ from 17.4 by more than 10 percent.

The character of the experimental curve of reflected intensities from glass suggests that the coefficient of absorption should be considerably larger than

17.4. Although theoretical curves were drawn for which larger values of a were assigned none could be found from Eq. (1) which duplicated the form of the experimental curve, although the "fit" was much closer than that indicated in the figure. It is possible, however, that the absorption coefficient of the surface layer, that in which the phenomenon of reflection takes place, is greater than the average value of the glass as a whole. Undoubtedly deviations of the surface from being optically flat would alter the form of the curve. The most nearly flat specimen used, however, gave no appreciably different result from the poorest mirror.

The results from the silver mirror show a better agreement between theory and experiment than those obtained from glass.

Here also the experimental results indicate a larger absorption coefficient than that measured. The silver film was not sufficiently thick to give a critical angle equal to that which would have been obtained with a thicker film.[6] This factor would seem to give a smaller coefficient of absorption rather than a larger one.

The results shown for platinum indicate good agreement between experimental and theoretical results. Just why there should be an agreement in this case and not in the other two is not clear. The writer plans to continue the investigation and hopes to be able to find an explanation for this behavior.

[6] Stauss, Phys. Rev. **34,** 1021 (1929), and also Edwards Phys. Rev. **32,** 712 (1929).

INTENSITY MEASUREMENTS IN THE SPECTRUM OF MANGANESE*

By Raymond S. Seward
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Abstract

Relative intensity measurements have been made for the lines of twenty-five multiplets of manganese, containing about one hundred and fifty lines in all. All but three of these were of Mn I. None of the Mn II multiplets measured were found to contain lines of abnormal intensity. On the other hand, at least eight multiplets of Mn I contain lines which are clearly anomalous. These eight multiplets contain a large number of the strongest lines of the spectrum. All involve terms derived from the term a^5D of Mn II and are of the inverted type with wide separations between the subterms. There seems to be regularity in the departure from normal intensities which can best be described by graphs in which the calculated intensities are plotted against the measured intensities on double logarithmic paper. In these plots, the satellites often assume a regular pattern above or below the main diagonal lines.

The total relative intensities of seventeen of these multiplets have also been measured. After reasonable excitation corrections have been applied, the agreement of their intensities with the theoretical values is as close as is to be expected. The measurements on the quartet triad of this group are the most reliable.

Introduction

THE elements of the iron group present complex spectra which are at present in the process of analysis.[1] A number of intensity studies have been made upon elements of this group, chiefly by Frerichs[2] at Bonn, by Harrison and co-workers[3] at Stanford, and by Ornstein and Bouma[4] at Utrecht.

The element manganese stands at the center of the iron group. Its maximum multiplicity is eight, which is the largest attained in this group. It is expected that departures from the Russell-Saunders or LS coupling which predominates in elements on the left side of the periodic table will gradually increase as the atomic number of the element in the group becomes greater, and at the same time departures from the normal intensity formulas will increase. Hesthal has found a greater fraction of anomalous lines in the multiplets of chromium ($Z=24$) than has Harrison in titanium (22), while the work of Ornstein and Bouma indicates still greater departures for cobalt (27) and nickel (28). The element manganese ($Z=25$) thus takes an interesting intermediate position in this connection.

* This work was done while the author was on leave of absence from the College of Puget Sound.

[1] H. N. Russell, Astrophys. J. **66**, 283–328, 347–438 (1927).

[2] R. Frerichs, Zeits. f. Physik **31**, 305 (1925); Ann. d. Physik **81**, 807 (1926).

[3] G. R. Harrison, J.O.S.A. **17**, 389 (1928). G. R. Harrison and H. Engwicht, J.O.S.A. **18**, 287 (1929). G. R. Harrison, J.O.S.A. **19**, 109 (1929). C. E. Hesthal, Ph.D. Thesis, Stanford University Library. Paper also reported at meeting of Am. Phys. Soc. Chicago, November 29–30, 1929, Paper No. 25. Abstract Phys. Rev. **35**, 126 (1930).

[4] L. S. Ornstein and T. Bouma, Phys. Rev. **36**, 679–693 (1930).

Considerable work has been done on the analysis of the spectrum of Mn I and a less amount on that of Mn II. The analysis of Mn I given by McLennan and McLay[5] and unpublished data furnished by Dunham of Mt. Wilson Observatory have been used in the present study. Material for Mn II has been taken from recent articles by Russell[6] and by Duffendack and Black.[7] The assignments of terms to definite electron configurations as given by Russell[8] and by Hund[9] is used.

The aim of the present investigation has been to secure accurate intensity determinations of as many lines of the spectrum of manganese as is practicable in order that the information may be available for reference in connection with atomic problems.

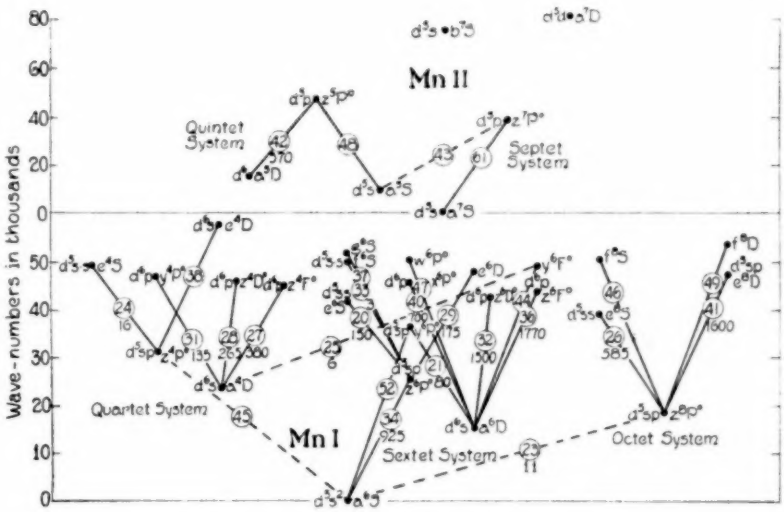

Fig. 1. Energy level diagram of the spectral terms of Mn I and Mn II.

Some features of the manganese spectra are summarized in Fig. 1, which is an energy level diagram of the spectral terms. They are classified according to multiplicity, there being quartet, sextet, and octet terms of Mn I and quintet and septet terms of Mn II. The separations of sub-terms are not shown. Symbols for electron configurations where known are written in front of the term symbols. Lines are drawn between terms to indicate multiplets. These are identified by numbers written in circles drawn on the lines, the larger numbers being assigned to the shorter wave-lengths. Intersystem transitions are represented by dotted lines.

Multiplets 27, 28, and 31 constitute a quartet triad, while multiplets 32, 36, and 40 make up a sextet triad. All six multiplets are due to *sp* electron

[5] J. C. McLennan and A. B. McLay, Trans. Roy. Soc. Canada **III,** 89 (1926).
[6] H. N. Russell, Astrophys. J. **66,** 233–255 (1927).
[7] O. S. Duffendack and J. R. Black, Phys. Rev. **34,** 35–43 (1929).
[8] H. N. Russell, Astrophys. J. **66,** 283–328, 347–438 (1927).
[9] F. Hund, Linienspectren, Julius Springer, Berlin, 1927, p. 181.

jumps and constitute two related super multiplets. Russell has shown that similar *sp* jumps are responsible for important triads in other members of the iron group.[10] All of the eight terms involved in these supermultiplets are inverted and will be referred to as the inverted system of terms, while most of the other terms of Mn I are normal. It is in members of this supermultiplet that the most interesting intensity results were found in the present study.

Experimental Procedure

The method of photographic photometry of spectral lines used in the present study has been described thoroughly in an article by G. R. Harrison.[11] The general method of procedure will not be given, but only special details noted.

The source used was an arc whose cathode consisted of a purified carbon rod into a cavity of which had been introduced finely pulverized manganese. For the anode a silver rod was used, as this gave a more steady arc than a second carbon rod, there being no serious overlapping of the silver lines with those of manganese.

Some spectrograms on each plate were exposed with an arc run at atmospheric pressure, while for others the pressure was reduced to from 10 to 20 cm of mercury. Currents of from 0.5 to 3.0 amperes were employed in order to give variable conditions of self-reversal and excitation and to bring out the strong and weak lines at the best intensities for measurement.

The source used for calibration in the ultraviolet was a mercury arc in quartz operated by a 110 volt storage battery, while in the visible a gas-filled 6 volt, 20 ampere tungsten lamp with a ribbon filament was used. As a standardizing source for much of the ultraviolet as well as all of the visible, a "black body" electric furnace with quartz window operated at about 2400°C was employed (see page 290 of reference 9), the intensities for various wave-lengths being determined by Wien's Law.

For varying the intensity during calibration, neutral wire screens were used whose transmitting power had been previously determined by thermopile readings.

The spectrographic arrangement, as in previous studies, was of a modified Paschen type. The lens for focusing the source on the slit was a quartz fluorite achromat of 2.5 cm aperture and a focal length remarkably constant at about 25 cm for all wave-lengths encountered. The grating was a concave reflector of about 35 feet radius, containing about 85,000 lines, 5900 per cm, the dispersion in the first order being about 1.67 A. per mm. This grating is remarkably free from ghosts, has intense first and second order spectra, and is in general excellent for intensity work.

The plates used, except for the region λλ 5300–6000, were the Eastman 36 brand. To secure measurable spectrograms for the green and yellow regions with the same exposure times as were used for the more actinic regions, panchromatic plates sensitized with ammonia were employed. Such plates, while

[10] See reference 1.

[11] G. R. Harrison, J.O.S.A. **19**, 267 (1929).

comparatively sensitive, are apt to become fogged and mottled. Their contrast was found much greater than desired, and the measurements made by their use are not so reliable as the others.

Self-reversal seems to have been reduced to a negligible amount in most cases, as indicated by a 45° slope to the "self-reversal curve" for a multiplet.[12] Exceptions in which self-reversal corrections were added are noted in the discussion of results.

Six sets of plates were secured, two of which covered the entire available spectrum (λλ 2500–6000). From 12 to 18 measurable spectra were obtained on

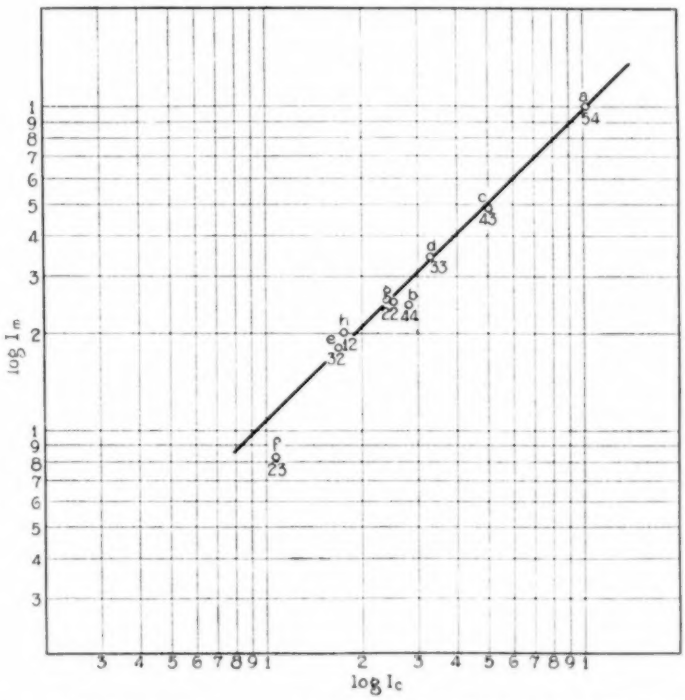

Fig. 2. Calculated and measured intensities for Multiplet 21 ($a^6D - y^4P$).

each plate. The results (recorded in the Table of Results) were obtained by averaging what were considered the most reliable determinations. It was impossible to measure accurately the weaker lines in certain exposures and in others the stronger lines were too black for accurate determination. But from 20 to 60 determinations were made for all but a few inaccessible lines.

Results and Discussion

Intensities within multiplets. The intensities of the lines making up a given multiplet may be determined with much greater accuracy than is possible when lines of different multiplets are compared, because excitation conditions

[12] In a self-reversal curve, the measured intensities are plotted against the calculated intensities on double logarithmic paper. For an explanation of such curves see p. 401 of the first reference cited in reference 3.

are similar for the various lines, and the plate sensitivity generally does not differ greatly for the lines being compared.

The results of the relative intensity measurements for the individual multiplets are found in column 5 of the Table of Results; the corresponding calculated intensities appear in column 4; while the results obtained by Frerichs for five multiplets which he measured appear in column 6. In all cases the intensity is expressed in percent of the strongest line. For convenience in testing the Sum Rule, the sums of the line intensities from a given upper state and of those having a given lower state have also been determined. These appear in the same column as the line intensities. Column 3 gives the term or transition distinguishing the sum or line.

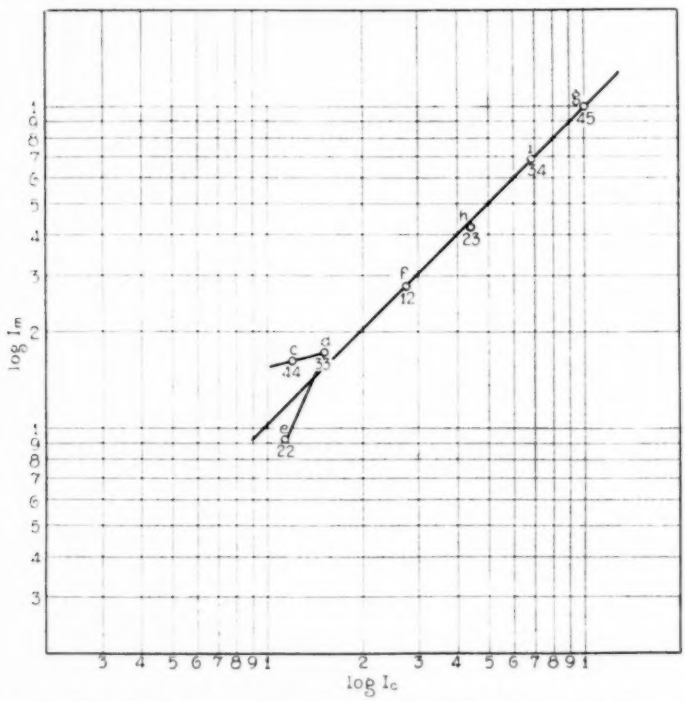

Fig. 3. Calculated and measured intensities for Multiplet 27 ($a^4D - z^4F$).

The measurements for the most interesting individual multiplets will now be discussed, following the order of decreasing wave-length.

Multiplet 21 ($a^6D - y^6P$; λλ 5540–5340). Besides lying in a region to which the ordinary photographic emulsion is insensitive, this multiplet covers a wide wave-length range in which the sensitivity of the panchromatic plate has a number of maxima and minima. It was also necessary to use exposures which were not favorable to complete removal of self-reversal. In obtaining the tabular values, self-reversal corrections were applied in some cases. The results indicate that lines *b* and *f* are abnormally weak. The multiplet is of interest in that its upper state belongs to the normal system of terms, while its lower state belongs to the inverted system. The calculated and measured intensities are shown graphically in Fig. 2.

Multiplet 23 (a^6S-z^8P; λλ 5432–5395). The two lines in this intersystem multiplet are fairly strong. Although there is no theoretical relation known between the intensities of such lines, the present measurements illustrate that the lines of largest J values are the strongest, and that the intensities follow qualitatively rules similar to those for lines in normal multiplets.

Multiplet 25 ($a^4D_3-z^6F_4$, $a^4D_4-z^6F_5$; λ 5000) and *Multiplet 45* (a^6S-z^4P; λ 3220) gave similar results.

Multiplet 27 (a^4D-z^4F; λλ 4766–4671). A large number of very consistent determinations were made on multiplet 27 in which self-reversal graphs showed a uniform slope of 45°, indicating the vanishing of this effect. The averaged values taken from the Table of Results are plotted in Fig. 3. A

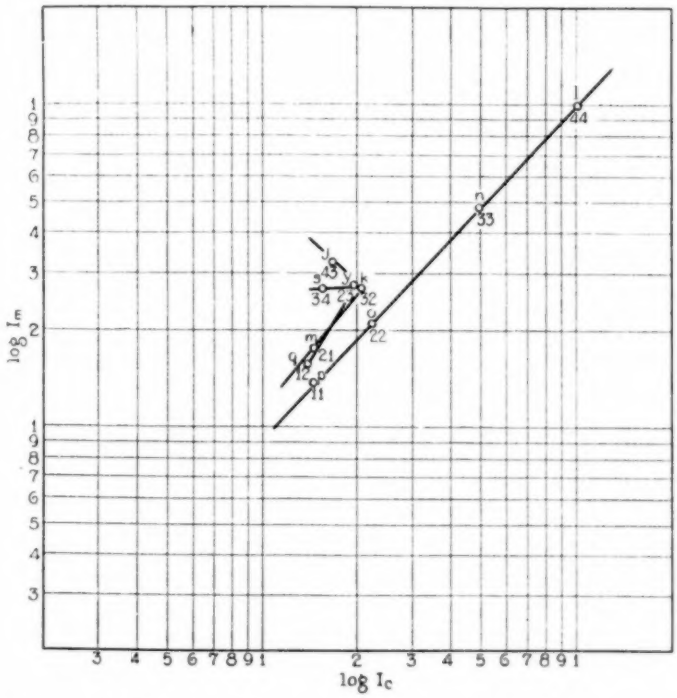

Fig. 4. Calculated and measured intensities for Multiplet 28 (a^4D-z^4D).

large number of similar graphs for the individual exposures showed an almost identical structure. While the four brightest lines are seen to have intensities very close to their calculated values, this is not the case for the first order satellites, line *c* being much too bright, line *d* less so, while line *e* is too weak. The wide divergence of lines *c* and *e* which are of nearly equal calculated intensity, is most striking.

Multiplet 28 (a^4D-z^4D; λλ 4502–4415). This multiplet is a second member of the triad to which multiplet 27 belongs. It is also one of the five manganese multiplets measured by Frerichs. As in the previous case, a large number of consistent determinations was made. The plot of the calculated and measured intensities on double logarithmic paper is shown in Fig. 4.

Both groups of satellites show very striking departures from the normal, being too bright by varying amounts. There are eight lines of fairly nearly equal calculated intensity in this multiplet, so that departures from the normal intensity could not very well be explained by self-reversal, even if some were present. An excitation correction would not tend to lessen the departures of the lines, since the lines which are too bright do not have a common upper state.

Multiplet 29 ($z^6P - e^6D$; λλ 4462–4455). This is the most satisfactory example of a multiplet belonging to the normal system of Mn I as distinguished from the inverted system. All the lines except *t* and *u* were resolved. The

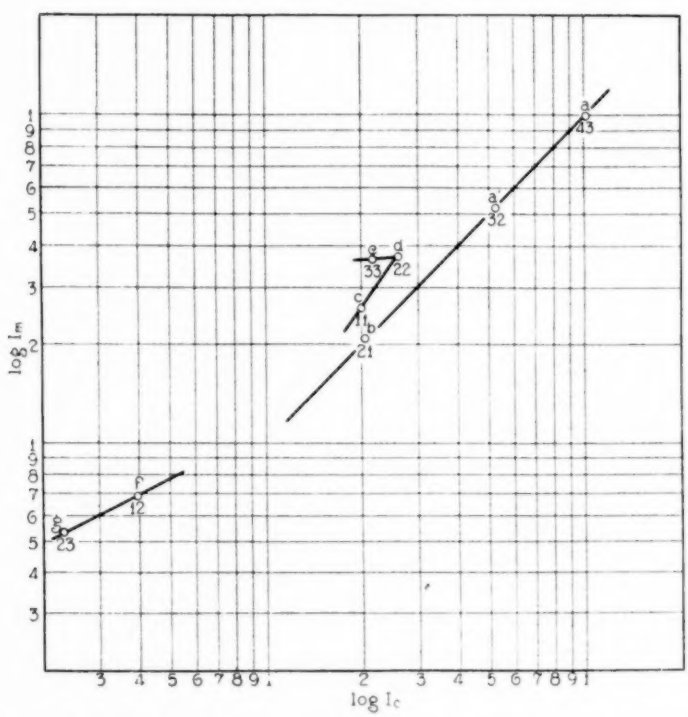

Fig. 5. Calculated and measured intensities for Multiplet 31 ($a^4D - y^4P$).

determinations showed excellent consistency and agreement with the calculated values. Frerichs obtained similar results.

Multiplet 31 ($a^4D - y^4P$; λλ 4312–4235). Multiplet 31, plotted in Fig. 5, is the third member of the quartet triad. As in the case of multiplet 28, the first order satellites are too bright; also lines *c* and *e* of nearly equal calculated intensities differ widely in measured intensities. The two second order satellites appear somewhat too bright and of more nearly equal intensities than their calculated values, although these lines were too weak for best determination. Frerichs obtained similar results in this case also.

Multiplet 32 ($a^6D - z^6D^0$; λλ 4084–4018). This is the first member of the sextet triad belonging to the *sp* inverted supermultiplet. Fig. 6 shows some

of the satellites too weak as compared with the main diagonal lines. This is in contrast to the corresponding DD^0 quartet multiplet 28, in which the corresponding lines were too intense. Lines *j* and *k* were not resolved completely. Their sum was measured, and then this value was distributed to the two lines in a ratio equal to the apparent intensities given when they were partly resolved. The position of these two individual lines is not known exactly, but their sum is not so great as the calculated value of the sum. This is another case in which departure from calculated values could not be explained by self-reversal, since a number of lines of nearly equal calculated intensities give radically different measured values.

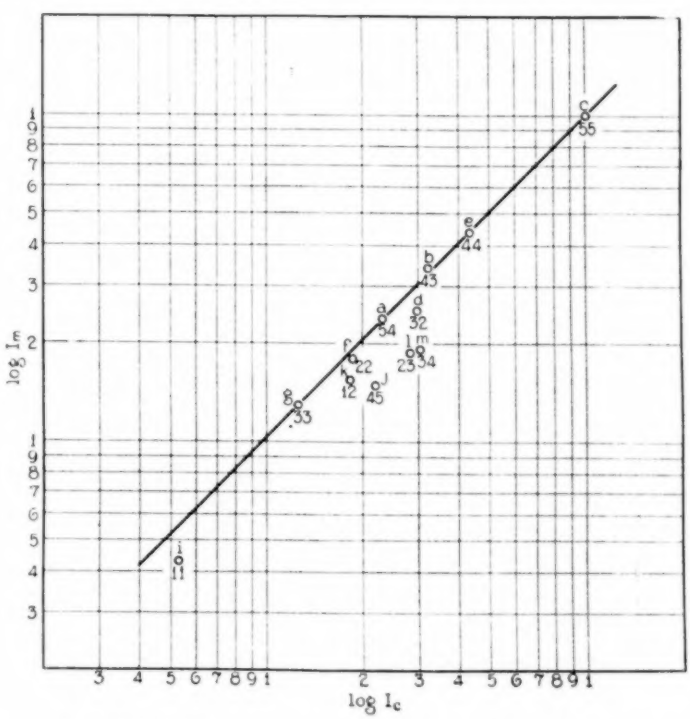

Fig. 6. Calculated and measured intensities for Multiplet 32 ($a^6D-z^6D^0$).

Multiplet 36 (a^6D-z^6F; λλ 3844–3776). When conditions were best for removal of self-reversal, cyanogen bands were apt to develop in the position occupied by multiplet 36. In order to resolve two pairs of interesting lines, it was also necessary to work in the second order. For these reasons, exposures in which some self-reversal remained were used in calculating the intensities, a small correction being applied to correct for the effect. The plot of the intensities as shown in Fig. 7 would be very similar if this correction had not been applied, except that the slope of the curve would be less. The departures from normal intensities are in this case the clearest and most regular of any so far encountered. The first order satellites are all clearly too weak as compared with the main diagonal lines. Since the lines are too weak, there

is no possibility of explaining their deviations by laps with unidentified lines. The two second order satellites *f* and *i* seem to have the order of their intensities inverted, though the data so far as this is concerned are not conclusive.

Multiplet 40 ($a^6D - x^6P$; λλ 3629–3577). This multiplet completes the *sp* sextet triad and is the last member of one of the supermultiplets arising from the a^5D term of Mn II. Measurements were possible in which self-reversal was apparently completely eliminated, and a large number of determinations gave nearly identical results. Of the first order satellites, line *d* is much too intense, line *e* slightly so, and line *f* is apparently about normal. The second order satellites *g*, *h*, *i* seem to be abnormally bright; these latter form a line in Fig. 8 which has much less slope than the main diagonal line.

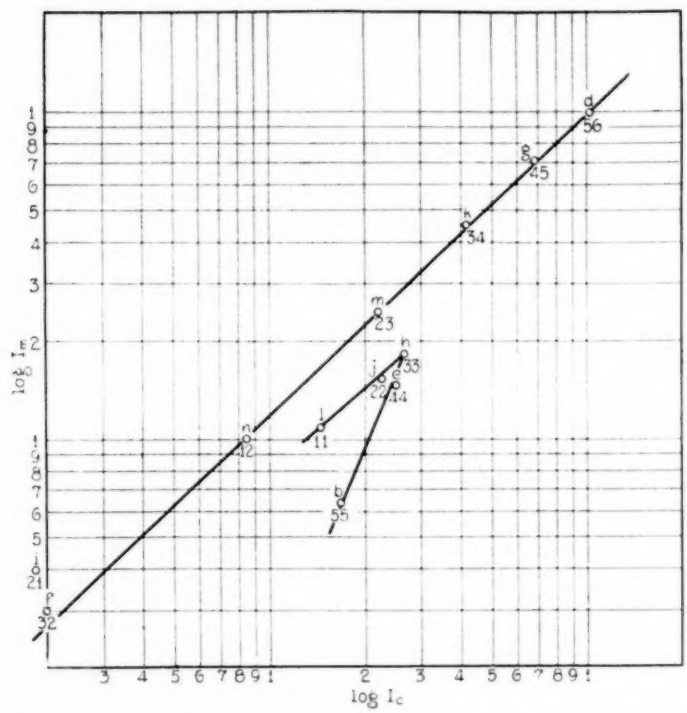

Fig. 7. Calculated and measured intensities for Multiplet 36 ($a^6D - z^6F$).

Multiplet 42 ($a^5D - z^5P$; λλ 3497–3442). This was the only complex multiplet of Mn II available for measurement. All measurements gave excellent agreement with the calculated values.

Multiplet 44 ($a^6D - y^6F^0$; λλ 3260–3209). Because of its comparative weakness, this multiplet, like its prototype number 36, was measured from exposures which had some self-reversal. The plot of its intensities shown in Fig. 9 is almost a reproduction of that for number 36, except that line *f* is a little depressed. Although the departure from normal intensities by the first order satellites is of the same type as in number 36 the amount of this departure is somewhat less. The second order satellites seemed to be stronger than their calculated values.

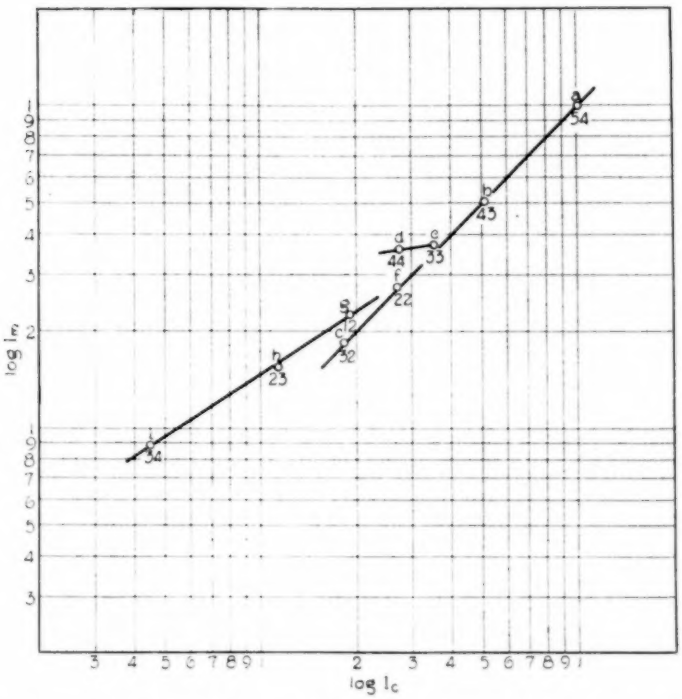

Fig. 8. Calculated and measured intensities for Multiplet 40 ($a^6D - x^6P_4$).

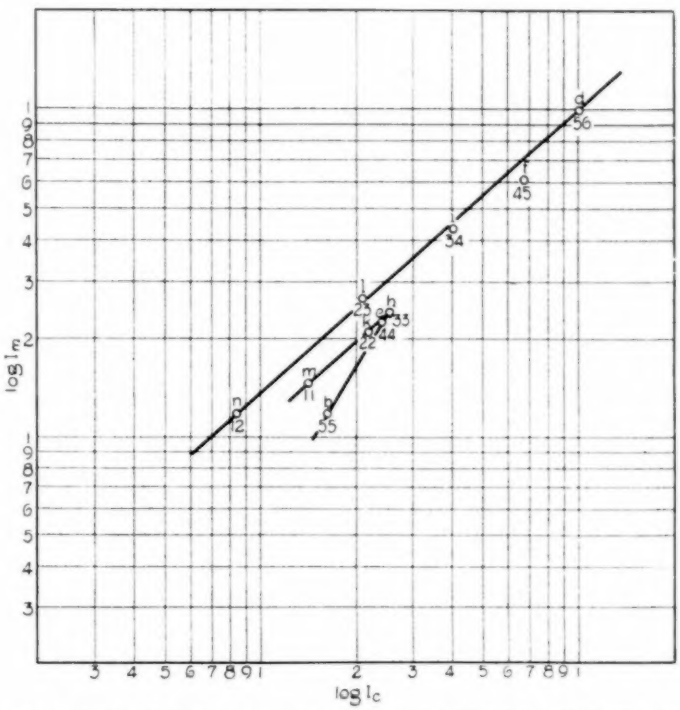

Fig. 9. Calculated and measured intensities for Multiplet 44 ($a^6D - y^6F^0$).

Multiplet 46 ($z^8P - f^8S$; λλ 3178–3148). Multiplet 46 gave very close agreement with the calculated values. It is the second member of a sharp series following a Rydberg formula, multiplet 26 being the first member.

Multiplet 47 ($a^6D - w^6P$; λλ 3082–3044). This has the same final state as has number 40. While the upper state has not been assigned to any electron configuration, it has normal intensities or nearly so (Fig. 10), and does not show anomalies analogous to those in number 40.

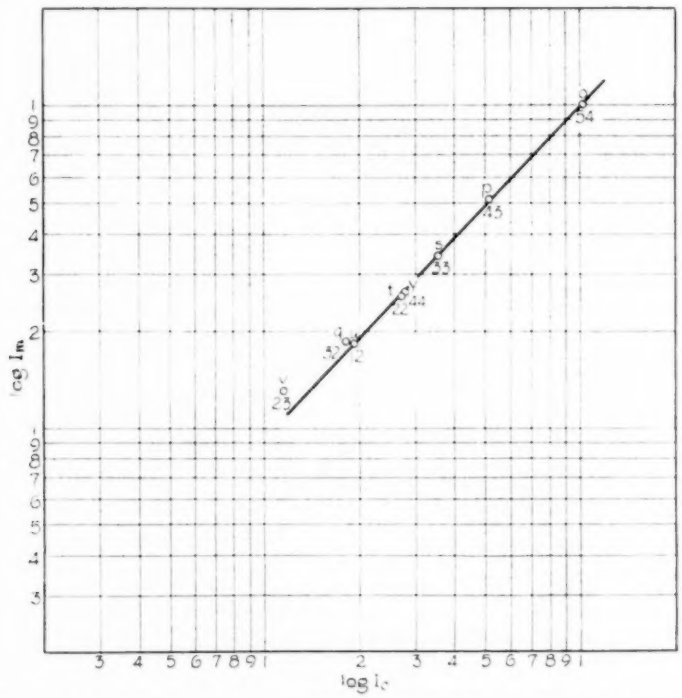

Fig. 10. Calculated and measured intensities for Multiplet 47 ($a^6D - w^6P$).

Multiplet 49 ($z^8P - f^8D$; λλ 2940–2914). Measurements indicated the normal intensity ratio between lines *b* and *a*. Line *c* was a little strong, probably due to a lap.

In summarizing the line intensities within multiplets, it may be stated that most of the anomalous lines, if not all of them, were in multiplets whose terms, one or both, were derived from the a^5D term of Mn II. The departure from normal intensities shown in graphs of Figs. 2 to 10 are of a regular nature in some cases at least. It is always possible to draw a straight line which passes through or near each point representing a main diagonal spectral line. Such lines can also be drawn through some of the satellite points, but the latter line is usually broken in the middle. One may proceed along this broken line in the shape of a *V* with the *J* values (subscripts) increasing or decreasing in regular sequence. Lines l_{11}, j_{22}, h_{33}, e_{44}, and b_{55} of multiplet 36 illustrate this regularity. It seems probable that this regular departure is caused by some perturbation factor which is usually negligible but which assumes significant values in the present case.

Relative intensities of the multiplets. Intensities for different multiplets, even when related, depend greatly on excitation conditions; so that measurements obtained under one set of conditions may not be compared directly with those obtained under another set. The figures for relative line and multiplet intensities given in column 7 of the Table of Results are based mainly on measurements made under fairly uniform conditions; namely, a current of 1.0 ampere and a pressure of 18 cm of mercury. Figures for each exposure were worked out separately and reduced to a common standard before finding the average figure which appears in column 7.

To obtain the intensities for infinite excitation as given in column 9, it was necessary to find the equivalent temperature. For this purpose the theoretical intensities of the members of the *sp* supermultiplet were employed.

The numbers 14, 10, 6, 15, 21, 9 are the intensities of multiplets 27, 28, 31, 32, 36, and 40 respectively as calculated by formula. The calculated intensities for the lines in each multiplet were first adjusted so that their sums were proportional to these numbers. The proper ν^4 correction was applied for each line, and the results placed in column 8 of the Table of Results.

If the multiplets may be brought to their calculated intensities by excitation correction, the equation $\log_{10}R = 0.625\Delta\sigma/T$ must have a common temperature solution. R is the factor required to bring the relative intensity of a line, or group of lines of common upper state, to the value for infinite excitation, and $\Delta\sigma$ is the difference in term values of the upper state in question and that of a line used as a standard.

In seeking the common solution of the above equation, the following procedure may be followed. The ratio I_m/I_c (measured intensity)/(calculated intensity) for each line group of common upper state is determined. The factor R_m by which each of these I_m/I_c values must be multiplied to make it equal to the value for the standard is next found. Finally the logarithms of these R_m values are plotted as ordinates and the corresponding $\Delta\sigma$ values as abscissas. In case these points all lie on a straight line, the intensities are normal, and the equivalent temperature may be found from the slope of this line; i.e., $T = 0.625\Delta\sigma/\log_{10}R$. In practice, a straight line which passes through as many such points as possible is drawn, the equivalent temperature and the corresponding excitation factors for different states being taken as determined by this line, the corrected measured intensities thus coming out greater or less than their calculated values according as their plotted points lie below or above the line.

In the present case, the first four multiplets had intensities which approximated their theoretical values quite closely, the equivalent temperature being between 5000 and 6000A. On the other hand, multiplets 36 and 40 had intensities which were much too small. These multiplets occur at wave-lengths about 3800A and 3600A respectively. It was thought that the apparent anomaly might be due to small J/I standardization values resulting from the action of scattered light. To test this point the values obtained when a filter was used which transmitted only ultraviolet light were tried for the members of the sextet triad, the quartet members being in a region not transmitted by

this filter. In this case the three multiplets showed fair alignment, although the calculated temperature tended to be a little less than in corresponding exposures for the quartet triad.

The measured intensities corrected for infinite excitation as recorded in column 9 of the Table of Results were obtained by first determining the relative intensities of the four multiplets of longest wave-length; then the relative intensities of the three short wave multiplets were determined from two exposures using the filter as just described. The two determinations were then tied together by multiplet 32 common to both sets. The intensities of other short wave multiplets in column 8 were also raised to correspond to these new determinations, the procedure being equivalent to a new standardization. From the preceding statements, it may be inferred that the determinations for the long wave-lengths are most reliable, and that it will be desirable to make further measurements in the ultraviolet in which more reliable standardizations for this region are available. This does not, however, affect the validity of line measurements in multiplets.

No total multiplet intensities for wave-lengths less than 3400A have been given, as intensity values for standardizing are not available at this time.

The approximate multiplet intensities as recorded in column 7 have also been written on Fig. 1, which may be used as a convenient means of studying the multiplet intensities as a whole. The values for the high upper states will be increased, of course, for higher equivalent temperatures or decreased for lower equivalent temperatures than that of the source here employed. It may be noticed that the sextet and quartet triads furnish a large part of the total radiation. Multiplet 41 in the octet system is very intense. Multiplet 34, furnishing the *raies ultimes*, while of very respectable intensity, is nevertheless surpassed by some of the others in total intensity. The comparatively small intensity of multiplet 21 as compared with that of number 40 with the same lower state and higher upper state is of interest. It may be recalled that number 21 has its lower state in the inverted system of terms and upper state in the normal system. Its comparative weakness may be connected with this fact. Multiplet 20, on the other hand, is much more intense than number 33 which has the same lower state. In this case, both the upper states, as well as the lower state, are of the normal type.

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TABLE OF RESULTS. *Summary of intensity measurements.*

Explanation

Column 1—Number of multiplet; distinguishing letter for each line.
Column 2—Approximate wave-length of the line.
Column 3—The transition for the spectral line or the term common to a line sum. Landé quantum numbers are used for the Mn I multiplets or for those of even multiplicity. Sommerfeld quantum numbers are used for Mn II multiplets. The first kind of quantum number is changed into the second by the subtraction of a half unit.

Column 4—Calculated intensity in percent of the strongest line.
Column 5—Measured intensity in percent of the strongest line.
Column 6—Intensity in percent of the strongest line as measured by Frerichs.
Column 7—Measured intensities reduced to a common standard (equivalent temperature about 5500 A, current 1.0 ampere, pressure 18 cm of Hg.
Column 8—Calculated intensities for six related multiplets reduced to a common standard.
Column 9—Measured intensities corrected for infinite excitation.

1 No.	Mul.	2 Wave-length	3 Trans.	4 I_c in %	5 I_m in %	6 I_f in %	7 I_m St.	8 I_c ∞	9 I_m ∞
20	*c*	6021.8	$z^6P^\circ_{3\frac{1}{2}}$–$a^6S$	100.0	100.0±		65.0		
	b	16.6	$z^6P^\circ_{2\frac{1}{2}}$–$a^6S$	75.2	75.5±		49.0		
	a	13.5	$z^6P^\circ_{1\frac{1}{2}}$–$a^6S$	54.3	53.0±		34.4		
20			Total	229.5	228.5		148.4		
21	*h*	5537.7	$a^6D_{3\frac{1}{2}}$–$y^6P^\circ_3$	17.3	20.2		5.7		
	g	16.8	$a^6D_{2\frac{1}{2}}$–$y^6P^\circ_2$	25.0	25.0		7.0		
	f	08.9	$a^6D_{1\frac{1}{2}}$–$y^6P^\circ_1$	10.6	8.3		2.3		
	e	5481.4	$a^6D_{3\frac{1}{2}}$–$y^6P^\circ_2$	16.8	18.3		5.1		
	d	70.6	$a^6D_{2\frac{1}{2}}$–$y^6P^\circ_3$	33.0	34.4		9.6		
	c[a]	57.5	$a^6D_{2\frac{1}{2}}$–$y^6P^\circ_2$	4.36	—		—		
	c	20.4	$a^6D_{1\frac{1}{2}}$–$y^6P^\circ_2$	49.5	48.3		13.5		
	b	01.4	$a^6D_{2\frac{1}{2}}$–$y^6P^\circ_1$	27.2	24.5		6.9		
	a	5341.1	$a^6D_{3\frac{1}{2}}$–$y^6P^\circ_2$	100.00	100.0		28.0		
			a^6D_4	100.0	100.0				
			a^6D_3	75.6	72.8				
			a^6D_2	54.1	57.0				
			a^6D_1	35.6	33.3				
			a^6D_0	17.3	20.2				
			$y^6P^\circ_4$	132.0	129.0±				
			$y^6P^\circ_3$	92.0	91.0				
			$y^6P^\circ_2$	58.0	63.5				
21			Total	283.0	283.4		79.0		
23	*n*	5432.6	a^6S–z^6P_3		62.7		4.4		
	m	5394.7	a^6S–z^6P_4		100.0		7.0		
23			Total		162.7		11.4		
24	*z*	5413.7	$z^4P^\circ_{2\frac{1}{2}}$–$a^4S$	32.5	34.2		2.7		
	y	5399.5	$z^4P^\circ_{1\frac{1}{2}}$–$a^4S$	65.8	64.0		5.1		
	x	77.6	$z^4P^\circ_{3\frac{1}{2}}$–$a^4S$	100.0	100.0		8.0		
24			Total	198.3	198.2		15.8		
25	*q*	5004.9	$a^4D_{3\frac{1}{2}}$–$z^4F^\circ_4$		63.0		2.3		
	p	4965.9	$a^4D_{2\frac{1}{2}}$–$z^4F^\circ_3$		100.0		3.7		
25			Total		163.0		6.0		4.5
26	*z*	4823.5	$z^6P^\circ_{3\frac{1}{2}}$–$a^6S$	100.0	100.0		240.0		
	y	4783.4	$z^6P^\circ_{2\frac{1}{2}}$–$a^6S$	82.6	82.5		198.00		
	x	61.5	$z^6P^\circ_{1\frac{1}{2}}$–$a^6S$	63.2	58.3		140.00		
26			Total	245.8	239.6		578.0		
27	*i*	4766.4	$a^4D_{3\frac{1}{2}}$–$z^4F^\circ_4$	68.0	69.0		92.7	92.6	92.7
	h	4765.9	$a^4D_{2\frac{1}{2}}$–$z^4F^\circ_3$	44.5	42.7		57.4	60.7	57.4
	g	62.4	$a^4D_{2\frac{1}{2}}$–$z^4F^\circ_2$	100.0	100.0		134.2	136.3	134.2
	f	61.5	$a^4D_{1\frac{1}{2}}$–$z^4F^\circ_2$	27.8	27.9		37.5	38.0	37.5
	e	39.1	$a^4D_{2\frac{1}{2}}$–$z^4F^\circ_3$	11.4	9.3		12.6	15.6	12.6
	d	27.5	$a^4D_{1\frac{1}{2}}$–$z^4F^\circ_2$	15.3	17.3		23.2	20.8	23.2
	c	09.7	$a^4D_{2\frac{1}{2}}$–$z^4F^\circ_4$	12.1	16.3		21.9	16.5	21.9
	b	01.2	$a^4D_{1\frac{1}{2}}$–$z^4F^\circ_3$	.85	.7±		.94	1.15	.94
	a	4671.7	$a^4D_{2\frac{1}{2}}$–$z^4F^\circ_2$	.6	.6±		.81	.82	.81
			a^4D_4	113.	116.9			153.6	
			a^4D_3	84.	87.0			114.6	
			a^4D_2	56.	52.0			76.1	
			a^4D_1	27.8	27.9			38.	
			$z^4F^\circ_4$	100.0	100.0		134.2	136.3	134.2
			$z^4F^\circ_3$	80.0	85.3		114.6	109.1	114.6
			$z^4F^\circ_2$	60.3	60.6		81.4	82.3	81.4
			$z^4F^\circ_1$	39.7	40.05		51.0	54.7	51.0
27			Total	280.0	286.0		381.25	382.0	381.25

1 No.	Mul.	2 Wave-length	3 Trans.	4 I_c in %	5 I_m in %	6 I_f in %	7 I_m St.	8 I_c ∞	9 I_m ∞
28	*s*	4502.2	$a^4D_2z^4D'_4$	15.6	27.0	24.5	21.6	19.2	32.4
	r	4498.9	$a^4D_3z^4D'_3$	19.7	27.6	23.6	22.1	24.2	36.1
	q	90.1	$a^4D_1z^4D'_2$	14.0	15.7	14.5	12.6	17.2	18.8
	p	72.8	$a^4D_1z^4D'_1$	14.4	13.9	12.4	11.1	17.5	16.7
	o	70.1	$a^4D_2z^4D'_2$	22.6	21.0	17.6	16.8	27.8	25.2
	n	64.7	$a^4D_3z^4D'_3$	49.5	48.0	40.5	38.4	61.0	57.6
	m	53.0	$a^4D_2z^4D'_1$	14.5	17.3	15.7	13.8	17.8	20.7
	l	51.6	$a^4D_4z^4D'_4$	100.	100.0	100.	80.0	123.	120.0
	k	36.4	$a^4D_3z^4D'_2$	20.8	27.2	25.4	21.8	25.6	32.6
	j	14.9	$a^4D_4z^4D'_3$	16.9	32.4	26.6	25.9	20.8	39.8
			a^4D_4	116.9	132.4	126.6		143.8	
			a^4D_3	85.9	102.0	90.4		105.8	
			a^4D_2	56.8	65.9	56.9		69.8	
			a^4D_1	28.4	29.6	26.9		34.7	
			$z^4D'_4$	115.6	127.0	124.5	101.6	142.2	152.4
			$z^4D'_3$	86.1	108.0	90.7	86.4	106.	133.5
			$z^4D'_2$	57.4	63.9	57.5	51.2	70.6	76.6
			$z^4D'_1$	28.9	31.1	28.1	24.9	35.3	37.4
28			Total	288.0	330.0	300.8	264.1	354.1	400.0
29	*B*	4462.0	$z^6P'_4e^6D_5$	100.0	100.0	100.0	57.0		
	∞	61.1	$z^6P'_4e^6D_4$	28.6	29.1	26.9	16.6		
	z	60.4	$z^6P'_3e^6D_3$	4.76	6.8±	4.64	3.9		
	y	58.3	$z^6P'_3e^6D_4$	51.6	51.8	51.8	29.6		
	x	57.6	$z^6P'_2e^6D_2$	36.6	37.9	37.2	21.1		
	w	57.0	$z^6P'_4e^6D_5$	12.0	11.6	11.4	6.6		
	v	55.8	$z^6P'_3e^6D_3$	18.6	18.4	17.3	10.5		
	u	58.3	$z^6P'_2e^6D_2$	28.5	27.8	26.9	15.8		
	t	55.0	$z^6P'_1e^6D_1$	20.1	22.7	18.9	12.9		
			$z^6P'_4$	133.4	135.9	131.5			
			$z^6P'_3$	100.2	100.4	100.4			
			$z^6P'_2$	67.22	68.9	63.1			
			e^6D_5	100.0	100.0	100.0			
			e^6D_4	80.2	80.9	78.7			
			e^6D_3	60.0	62.4	59.1			
			e^6D_2	40.5	39.4	38.3			
			e^6D_1	20.1	22.7	18.9			
29			Total	300.8	305.2	295.0	174.0		400.0
31	*g*	4312.6	$a^4D_2Y^4P'_2$	2.32	5.4±	6.7	2.5	2.44	5.2
	f	4284.1	$a^4D_1Y^4P'_2$	3.94	6.9±	7.1	3.3	4.14	6.7
	e	81.1	$a^4D_2Y^4P'_1$	21.4	36.4	34.6	17.2	22.5	35.4
	d	65.9	$a^4D_2Y^4P'_2$	25.8	37.3	32.5	17.6	27.1	36.3
	c	57.7	$a^4D_1Y^4P'_1$	20.0	26.2	23.4	12.8	21.05	25.5
	b	39.7	$a^4D_2Y^4P'_1$	20.6	21.0	20.8	9.8	21.7	20.4
	a	35.3	$a^4D_4Y^4P'_2$	100.0	100.0	100.0	47.1	105.0	97.2
	a	35.1	$a^4D_3Y^4P'_2$	62.3	52.3	52.3	24.7	54.9	51.0
			a^4D_4	100.0	100.0	100.0		105.0	
			a^4D_3	73.7	88.7	87.1		77.4	
			a^4D_2	48.7	63.7	60.0		51.2	
			a^4D_1	23.9	33.1	30.5		25.2	
			$y^4P'_3$	123.7	141.8	141.3	66.8	129.9	137.8
			$y^4P'_2$	82.0	96.5	92.1	45.6	86.1	94.0
			$y^4P'_1$	40.6	47.2	44.2	22.6	42.7	45.9
31			Total	246.3	285.5	277.6	139.8	258.8	277.7
32	*m*	4083.6	$a^6D_2z^6D^0_4$	30.2	19.2	23.0	87.0	65.1	42.8
	l	82.9	$a^6D_2z^6D^0_3$	28.5	19.0	21.7	86.0	61.0	42.3
	k	79.4	$a^6D_1z^6D^0_2$	18.2	15.5	15.0	70.0	39.0	34.5
	j	79.2	$a^6D_2z^6D^0_5$	21.6	15.0	15.0	68.0	46.1	33.4
	i	70.3	$a^6D_1z^6D^0_1$	5.3	4.3	4.3	19.5	11.4	9.6
	h	68.0	$a^6D_2z^6D^0_2$	.53	1.1±	.5	5.0	1.14	2.4
	g	63.5	$a^6D_2z^6D^0_3$	12.3	13.1	13.5	59.4	26.4	29.2
	f	58.9	$a^6D_2z^6D^0_1$	18.6	18.1	16.8	82.0	39.8	40.3
	e	55.6	$a^6D_4z^6D^0_4$	43.5	43.9	45.0	198.5	93.0	97.5
	d	48.8	$a^6D_3z^6D^0_3$	29.4	25.1	29.4	113.8	63.0	55.9
	c	41.4	$a^6D_4z^6D^0_5$	100.0	100.0	100.0	454.0	214.0	222.0
	b	35.7	$a^6D_4z^6D^0_3$	32.0	34.3	30.9	155.0	68.4	76.1
	a	18.1	$a^6D_3z^6D^0_4$	22.9	24.0	23.5	109.0	49.0	53.5
			a^6D_4	122.9	124.0	123.5		263.0	
			a^6D_4	97.1	93.2	90.9		207.5	
			a^6D_3	71.9	57.4	65.9		154.5	
			a^6D_2	47.6	38.2	39.		101.9	
			a^6D_1	23.5	19.8	19.3		50.4	
			$z^8D^0_5$	121.6	115.0	115.0	522.0	260.1	255.4

1 No.	Mul.	2 Wave-length	3 Trans.	4 I_e in %	5 I_m in %	6 I_f in %	7 I_m St.	8 I_e ∞	9 I_m ∞
			$z^6D^0_4$	96.6	87.1	91.5	394.5	207.1	193.8
			$z^6D^0_3$	72.8	66.4	66.1	300.4	155.8	147.6
			$z^6D^0_2$	48.1	41.7	44.9	188.8	103.1	92.8
			$z^6D^0_1$	23.9	22.4	21.1	101.5	51.2	49.9
32			Total	363.0	332.6	338.5	1507.0	777.3	739.5
33	*r*	4061.7	$z^6P^0_3/^6S$	100.0	100.0±		1.2		
	q	4059.4	$z^6P^0_2/^6S$	75.0	74.2±		.9		
	p	4057.96	$z^6P^0_1/^6S$	50.0	50.6±		.6		
33			Total	225.0	224.8		2.7		
34	*z*	4034.5	$a^6Sz^6P^0_2$	50.0	60.0		206.0		
	y	33.1	$a^6Sz^6P^0_3$	75.0	87.5		309.0		
	x	30.8	$a^6Sz^6P^0_4$	100.0	100.0		412.0		
34			Total	225.	247.5		927.0		
36	*n*	3844.0	$a^6D_1z^6F^0_2$	8.27	10.1		55.0	33.1	41.0
	m	41.1	$a^6D_2z^6F^0_3$	21.2	24.1		131.0	85.0	98.0
	l	39.8	$a^6D_3z^6F^0_4$	14.2	10.9		59.2	57.0	44.4
	k	34.4	$a^6D_1z^6F^0_1$	40.2	45.2		245.0	161.0	184.0
	j	33.9	$a^6D_2z^6F^0_2$	22.1	15.4		83.6	88.6	62.7
	i	29.7	$a^6D_3z^6F^0_3$	1.81	4. ±		21.7	7.2	16.3
	h	23.9	$a^6D_4z^6F^0_4$	26.0	18.3		99.0	104.0	74.5
	g	23.5	$a^6D_5z^6F^0_5$	66.0	71.1		386.0	264.0	289.0
	f	16.7	$a^6D_2z^6F^0_2$	1.97	3. ±		16.0	7.91	12.2
	e	09.6	$a^6D_3z^6F^0_3$	24.6	14.8		80.5	98.5	60.2
	d	06.9	$a^6D_4z^6F^0_4$	100.0	100.0		543.0	400.0	407.0
	c	3799.3	$a^6D_3z^6F^0_2$	1.36	(2)		11.0	5.45	8.1
	b	90.2	$a^6D_4z^6F^0_3$	16.4	6.5		35.2	65.5	26.4
	a	76.5	$a^6D_5z^6F^0_4$	.6	(1)		5.4	2.4	4.1
			a^6D_5	117.0	107.5			417.0	
			a^6D_4	92.0	87.9			368.0	
			a^6D_3	68.2	66.5			272.9	
			a^6D_2	45.1	45.1			180.8	
			a^6D_1	22.5	21.0			90.1	
			$z^6F^0_5$	100.0	100.0		543.0	400.0	407.0
			$z^6F^0_4$	82.4	77.6		421.2	329.5	315.4
			$z^6F^0_3$	65.4	61.0		330.9	261.9	248.3
			$z^6F^0_2$	48.6	44.4		241.0	194.5	180.6
			$z^6F^0_3$	32.4	28.5		154.6	129.6	115.9
			$z^6F^0_1$	16.0	14.9		80.9	64.2	60.7
36			Total	344.8	326.4		1770.0	1379.7	1328.0
38		3800.6	$z^4P^0_1c^4D_2$	100.0	100.0				
		3787.5	$z^4P^0_2c^4D_3$	53.6	40.0±				
		74.7	$z^4P^0_3c^4D_3$	23.2	15.0±				
38			Total	176.8	155.0				
40	*i*	3629.1	$a^6D_3x^6P^0_4$	4.5	8.9	13.3	19.7	11.5	23.8
	h	23.8	$a^6D_2x^6P^0_3$	11.4	15.5	23.6	34.4	29.1	41.4
	g	19.4	$a^6D_1x^6P^0_2$	19.2	22.3	32.8	49.5	49.0	58.5
	f	10.3	$a^6D_2x^6P^0_2$	27.4	27.3	40.0	60.5	70.0	72.8
	e	08.5	$a^6D_3x^6P^0_3$	35.3	37.0	50.3	82.0	90.3	98.8
	d	07.5	$a^6D_4x^6P^0_4$	27.6	35.9	48.7	79.7	70.7	95.8
	c	3595.1	$a^6D_3x^6P^0_2$	18.4	18.5	22.5	41.0	46.6	49.4
	b	86.5	$a^6D_4x^6P^0_3$	51.1	50.4	58.4	112.0	131.0	134.5
	a	77.9	$a^6D_5x^6P^0_4$	100.0	100.0	100.0	222.0	256.0	267.0
			a^6D_5	100.0	100.0	100.0		256.0	
			a^6D_4	78.7	86.3	107.1		201.7	
			a^6D_3	58.2	64.4	86.1		148.4	
			a^6D_2	38.8	42.8	63.6		99.1	
			a^6D_1	19.2	22.3	32.8		49.0	
			$x^6P^0_4$	132.1	144.8	162.0	321.4	338.2	385.6
			$x^6P^0_3$	97.8	102.9	132.3	228.4	250.4	274.7
			$x^6P^0_2$	65.0	68.1	95.3	151.0	165.6	181.7
40			Total	294.9	315.8	389.6	700.0	754.2	819.2

• Self-reversal not completely eliminated.

1 No.	Mul.	2 Wave-length	3 Trans.	4 I_c in %	5 I_m in %	6 I_f in %	7 I_m St.	8 $I_c \infty$	9 ${}_mI\infty$
41		3570.1	$z^5P^1_3 e^5D_4$	6.5					
		69.8	$z^5P^1_2 e^5D_4$	32.5					
		69.5	$z^5P^1_1 e^5D^4$	100.					
		48.2	$z^5P^1_3 e^5D_3$	18.5					
		48.0	$z^5P^1_2 e^5D_3$	43.2					
		47.8	$z^5P^1_1 e^5D_3$	52.2					
		32.1	$z^5P^1_3 e^5D_2$	34.8					
		32.0	$z^5P^1_2 e^5D_2$	33.4					
		31.8	$z^5P^1_1 e^5D_1$	19.0					
	w		$z^5P^0_3$	139.0					
	v		$z^5P^0_2$	113.0					
	u		$z^5P^0_1$	86.5			430.		
41			Total	338.5			1680.		
42	*h*	3497.5	$a^5D_1 z^5P^1_2$	7.8	7.7		16.2		
	g	96.8	$a^5D_2 z^5P^1_2$	3.5	3.9		8.2		
	f	95.8	$a^5D_0 z^5P^1_1$	10.4	10.3		22.0		
	e	86.6	$a^5D_1 z^5P^1_1$	23.6	23.6		49.5		
	d	82.9	$a^5D_2 z^5P^1_2$	31.0	30.5		64.0		
	c	74.1	$a^5D_3 z^5P^1_3$	18.7	19.0		40.0		
	c	74.0	$a^5D_2 z^5P^1_2$	25.0	25.4		53.4		
	b	60.3	$a^5D_1 z^5P^1_1$	50.0	50.1		105.2		
	a	42.0	$a^5D_0 z^5P^1_1$	100.0	100.0		210.0		
			a^5D_4	100.0	100.0				
			a^5D_3	75.0	75.4				
			a^5D_2	53.2	53.4				
			a^5D_1	31.4	31.3				
			a^5D_0	10.4	10.4				
			$z^5P^0_3$	128.5	129.3				
			$z^5P^0_2$	88.8	88.3				
			$z^5P^0_1$	52.7	53.0				
42			Total	270.0	270.6		568.5		
44	*n*	3260.2	$a^6D_1 y^6F^0_1$	8.3	11.8				
	m	58.4	$a^6D_1 y^6F^0_2$	14.2	14.7				
	l	56.1	$a^6D_2 y^6F^0_2$	21.1	26.6				
	k	52.9	$a^6D_2 y^6F^0_3$	22.0	21.0				
	j	51.1	$a^6D_3 y^6F^0_3$	.18	4.5±				
	i	48.5	$a^6D_3 y^6F^0_4$	40.3	43.8				
	h	43.8	$a^6D_3 y^6F^0_5$	25.8	24.1				
	g	40.6	$a^6D_4 y^6F^0_5$	.2	7. ±				
	f	36.8	$a^6D_4 y^6F^0_6$	66.5	61.7				
	e	30.7	$a^6D_4 y^6F^0_4$	24.1	22.6				
	d	28.1	$a^6D_5 y^6F^0_6$	100.0	100.0				
	c	26.0	$a^6D_4 y^6F^0_5$	.14	3. ±				
	b	12.9	$a^6D_5 y^6F^0_5$	16.4	11.9				
	a	06.9	$a^6D_5 y^6F^0_4$	.06	—				
			a^6D_5	117.0	112.0				
			a^6D_4	90.7	87.3				
			a^6D_3	66.9	74.9				
			a^6D_2	43.3	52.1				
			a^6D_1	22.5	26.5				
			$y^6F^0_6$	100.0	100.0				
			$y^6F^0_5$	82.9	73.6				
			$y^6F^0_4$	64.5	66.4				
			$y^6F^0_3$	47.0	53.7				
			$y^6F^0_2$	30.5	39.8				
			$y^6F^0_1$	14.4	19.2				
44			Total	339.3	352.7				
45	*g'*	3224.8	$a^6S z^4P^0_3$		100.0				
	x	17.0	$a^6S z^4P^0_2$		45.0				
45			Total		145.0				
46	*m'*	3178.5	$z^5P^1_3 f^5S$	100.0	100.0				
	m'	61.1	$z^5P^1_2 f^5S$	82.0	82.1				
	l'	48.2	$z^5P^1_1 f^5S$	62.2	62.6				
46			Total	244.2	244.7				

1 No.	Mul.	2 Wave-length	3 Trans.	4 I_c in %	5 I_m in %	6 I_f in %	7 I_m St.	8 $I_c \infty$	9 $I_m \infty$
47	*w*	3082.1	$a^6D_5w^6P^\circ_4$	4.55	lapped				
	v	81.3	$a^6D_5w^6P^\circ_3$	11.4	13.1				
	u	79.6	$a^6D_1w^6P^\circ_2$	19.2	18.3				
	t	73.1	$a^6D_5w^6P^\circ_2$	27.2	25.8				
	s	70.3	$a^6D_3w^6P^\circ_2$	35.2	34.4				
	r	66.0	$a^6D_4w^6P^\circ_3$	27.8	26.1				
	q	62.1	$a^6D_3w^6P^\circ_2$	18.2	18.7				
	p	54.4	$a^6D_2w^6P^\circ_1$	51.0	51.3				
	o	44.6	$a^6D_5w^6P^\circ_3$	100.0	100.0				
			a^6D_5	100.0	100.0				
			a^6D_4	78.8	77.4				
			a^6D_3	58.0	57.6				
			a^6D_2	38.6	38.9				
			a^6D_1	19.2	18.3				
			$w^6P^\circ_4$	132.4	130.6				
			$w^6P^\circ_3$	97.6	98.8				
			$w^6P^\circ_2$	64.6	62.8				
47			Total	294.6	292.2				
48	*z*	2949.2	$a^6S_2z^6P^\circ_3$	100.0	100.0				
	y	39.3	$a^6S_2z^6P^\circ_2$	73.0	72.2				
	x	33.1	$a^6S_2z^6P^\circ_1$	44.0	43.0				
48			Total	217.0	215.2				
49	*G*	2940.5	$z^5P^\circ_3f^5D$	100.0	100.0± (lap)				
	B	25.6	$z^5P^\circ_4f^5D$	81.3	81.3				
	A	14.6	$z^5P^\circ_3f^5D$	62.0	63.8				
49			Total	243.3	245.1				
52	*c*	2801.1	$a^5Sy^5P^\circ_3$	50.0	•100. ±				
	b	2798.3	$a^5Sy^5P^\circ_2$	75.0	90. ±				
	a	94.8	$a^5Sy^5P^\circ_4$	100.0	80. ±				
52			Total	225.0					
61		2605.7	$a^7S_3z^7P^\circ_2$	47.5	•100. ±				
		2593.7	$a^7S_3z^7P^\circ_3$	68.5	100. ±				
		76.1	$a^7S_3z^7P^\circ_4$	100.0	100. ±				
61			Total	216.0					

• Self-reversal; J/I uncertain.

RAMAN SPECTRA OF SOME ORGANIC HALIDES

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Abstract

Raman spectra obtained by helium excitation from nineteen organic compounds, $CHCl_3$, CH_3Br, CH_3MgBr, CH_3I, CH_3MgI, C_2H_5Cl, C_2H_5Br, C_2H_5I, $ClCH_2CH_2Cl$, $BrCH_2CH_2Br$, CH_3CHCl_2, CH_3CHBr_2, $C_2H_2Cl_4$, $C_2H_2Br_4$, C_6H_6, C_5H_5N, $C_6H_5CH_2Cl$, C_6H_5Cl, C_6H_5Br, five of which have not been reported on before, are described and discussed. It is shown that in many cases the observed frequencies can be expressed in terms of four assumed fundamentals (five in the cyclic compounds), two of which are not observed, and which may prove to be illusory. The bearing of such theory as is available is discussed.

THE Raman* spectra of a number of simple organic compounds containing carbon, hydrogen, and halogen (chlorine, bromine, or iodine) atoms are described and discussed in this paper. The work was begun as part of a systematic study of a number of physical properties of the class of compounds known as Grignard reagents, which are formed in anhydrous ether solution when the halogen compounds just mentioned react with magnesium to form compounds of the type R-Mg-X. Raman spectra from two such compounds are described below. At the time the work was started, only a few of the organic halides had been reported on; but since then, various workers have reported the Raman spectra of a great many of them, as will be noted below, and some steps have been made toward theoretical interpretation of the spectra.

Experimental Arrangements

In almost every case, the results reported by others have been obtained using light from a mercury arc, usually unfiltered, following an early scheme suggested by Wood.[1] The advantage of intense exciting light, which this method possesses, is compensated to a large extent by the serious overlapping of the Raman patterns from the numerous exciting lines, which leads to difficulty and error in identifying the exciting line responsible for certain displaced lines. Matters can be improved somewhat by using appropriate filters, as Wood has shown. The results in the present paper are free from such uncertainty, since they were obtained by helium excitation, using a helium spiral surrounding the "resonance" tube, and a tube of Corning red ultra

* No attempt is made to give here a complete bibliography of all the hundreds of papers that have appeared on the subject since the discovery of the effect was announced by C. V. Raman, Indian Jour. of Physics **2**, 387 (1928). Such bibliographies are available elsewhere; e.g., S. Bhagavantam, Ind. Jour. Phys. **5**, 237 (1930), A. S. Ganesan, Ind. Jour. Phys. **4**, 281 (1929), and the Symposium on Molecular Spectra, Trans. Faraday Soc. **25**, 611–949 (1929).

[1] R. W. Wood, Phil. Mag. (7) **6**, 729 (1928).

glass as a filter. This method is also due to Wood.[2] While the method has not the advantage of the high intensity obtainable from the newer helium arc,[3,4] it does have, in common with this apparatus, the great advantage that there is only one exciting line, λ3889, and almost no helium lines coming through the filter to confuse the Raman pattern. Further, this exciting line has a shorter wave-length than many of the mercury lines used. As shown by Ornstein and Rekveld,[5] the intensity of the Raman lines increases at least approximately with the fourth power of the exciting frequency. Besides the consequent gain in strength of the Raman lines, there is the added advantage that the displaced lines occur at wave-lengths near the sensitivity maximum of the photographic plates.

The first exposures were made using a "resonance" tube about an inch in diameter and twelve inches long. It was soon found that better results were obtained with a smaller tube, about 1 cm in diameter and 10 cm long, with a smaller filter and helium spiral; less power was required, too, and smaller quantities of the substances to be investigated. The spectra were photographed with a specially reconstructed single prism glass spectrograph of considerable speed, which has been described elsewhere.[6] For measurement, images of the spectra were projected, using a magnification of about forty diameters, on a screen on which a scale of wave-numbers had been worked out, using a large number of reference lines. With this scale, wave-number differences could be read off with an accuracy of about 5 cm^{-1} in the case of the sharpest lines. Many of the Raman lines are too broad, however, to permit reading as accurately as this.

Discussion of Results

In discussing Raman spectra, the quantity of primary interest is the amount by which a given line differs in frequency (or more usually, in wave-number) from the exciting line. Since the arrangements used permitted this quantity to be read directly, it is recorded in the tables that follow. In the tables, compounds of similar structures are grouped, for convenience in comparing their spectra. Intensities are indicated by numbers in parentheses following the observed wave-number shifts.

While measurements could be checked to about 5 cm^{-1}, it by no means follows that the results obtained by different observers will check as closely as this. In some cases the agreement is better, but in a considerable number, the disagreement is several times as large. There is very great need now for more accurate results than have been given in most of the investigations so far published. A single table is included to show the extent to which agreement is found in typical cases. In many cases the agreement is worse, owing to difficulty in identifying lines. Beyond this, it has seemed unnecessary to

[2] R. W. Wood, Phil. Mag. (7) **7**, 744 (1929).
[3] Reynolds and Benford, Rev. of Sci. Insts. **1**, 413 (1930).
[4] R. W. Wood, Phys. Rev. **36**, 1421 (1930).
[5] Ornstein and Rekveld, Zeits. f. Physik **61**, 593 (1930).
[6] R. T. Dufford, J. Opt. Soc. Am. **9**, 405 (1924).

TABLE I. (a) *Raman spectrum of chloroform, $CHCl_3$.*

Cleeton and Dufford	Dadieu and Kohlrausch 8, V	Ganesan and Venkateswaran 13	Pringsheim and Rosen 10	Bhagavantam and Venkateswaran 14
269 (3)	259 (6)	261 (5)	257 (4)	261 (4)
376 (3)	364 (5)	367 (6)	368 (4)	367 (5)
671 (3)	664 (5)	669 (6)	666 (4)	669 (4)
775 (3)	756 (4)	762 (3)	766 (3)	762 (3)
	1214 (2)	1218 (2)	1214 (2)	1218 (2)
		1441 (1)		1441 (1)
3015 (5)	3016 (3)	3019 (4)	3009 (2)	3019 (3)

(b) *Raman spectrum of benzene, C_6H_6.*

Daure 7	Cleeton and Dufford	Dadieu and Kohlrausch 8, I	Dadieu and Kohlrausch 8, II	Fujioka 9	Pringsheim and Rosen 10	Wood 12	Dadieu and Kohlrausch 8, IV	Soderqvist 11
610	621 (1)	605 (4)	607 (4)	607	615 (3)	606	602 (3)	604.6 (2)
842		848 (2)	846 (2)	849	867 (2)	849	844 (1)	849.1 (0)
991	1003 (20)	995 (10)	993 (10)	993	995 (4)	992	991 (10)	991.3 (5)
1178	1203 (3)	1183 (3)	1180 (3)	1182	1183 (3)	1178	1178 (3)	1179.0 (1)
			1363 (1/2)				1362 (1/2)	
		1481 (3)			1479 (2)			
1584	1619 (5)	1596 (3)	1588 (3)	1585	1591 (2)	1584	1586 (3)	1583.6 (1)
				1612	1605 (2)	1603	1603 (1)	1604.1 (1)
						2460		
						2542		
						2597		
						2617		
						2784		
						2928		
		2944 (5)	2947 (3)			2947	2945 (4)	2946.8 (2)
				3050		3046		3046.9 (1)
3060	3078 (50)	3058 (8)	3057 (5)	3060	3059 (3)	3060	3056 (8)	3061.3 (4)
						3164		3162.9 (1)
						3183		3184.8 (2)

republish all the results of other investigators; but references are given to all such work as is known to the writers.

In studying the Raman spectra of organic halides, one of the writers (C. E.C.), who made the wave-number measurements, discovered the existence of certain apparent regularities, the more important of which are indicated in the tables that follow. It would appear from these that it is possible to express the frequencies found in the Raman spectra of each of the aliphatic halides as combinations or overtones of four fundamental frequencies, of which usually two must be assumed to exist without being observed in the spectra themselves. In the tables, beginning with Table II, there is given for each substance the observed frequency differences in one column, and the

[7] P. Daure, An. d. Physique **12,** 375 (1929); C. R. **186,** 1833 (1928); **188,** 1492 (1929).

[8] Dadieu and Kohlrausch, Phys. Zeits. **30,** 384 (1929); Ber. **63** B, 251 (1930); Naturwiss. **17,** 366, 625 (1929);

[i] Monatsh. f. Chemie **52,** 220 (1929); Sitzb. Akad. Wiss. Wien (IIa) **138,** 41 (1929).

[ii] Monatsh. f. Chemie **52,** 379 (1929); Sitzb. Akad. Wiss. Wien (IIa) **138,** 335 (1929).

[iii] Monatsh. f. Chemie **52,** 396 (1929); Sitzb. Akad. Wiss. Wien (IIa) **138,** 419 (1929).

[iv] Monatsh. f. Chemie **53–54,** 282 (1929); Sitzb. Akad. Wiss. Wien (IIa) **138,** 607 (1929).

[v] Monatsh. f. Chemie **55,** 58 (1930); Sitzb. Akad. Wiss. Wien (IIa) **138,** 651 (1929).

[vi] Monatsh. f. Chemie **55,** 201 (1930); Sitzb. Akad. Wiss. Wien (IIa) **138,** 799, (1930).

[vii] Monatsh. f. Chemie **55,** 379 (1930).

[9] Fujioka, Sci. Papers Inst. Phys. and Chem. Res. Japan **II,** 205 (1929).

[10] Pringsheim and Rosen, Zeits. f. Physik **50,** 741 (1928).

[11] J. Soderqvist, Zeits. f. Physik **59,** 446 (1929–30).

[12] R. W. Wood, Phys. Rev. **36,** 1431 (1930).

[13] Ganesan and Venkateswaran, Ind. Jour. Phys. **4,** 195 (1929).

[14] Bhagavantam and Venkateswaran, Proc. Roy. Soc. **A127,** 360 (1930).

TABLE II. *Raman spectra of methyl halides.*

Methyl bromide CH_3Br	Methyl iodide CH_3I	Methyl magnesium bromide CH_3MgBr	Methyl magnesium iodide CH_3MgI	Assumed combinations
603 (10)	534 (10)	1131 (1)	1076 (1)	V_3
	1254 (3)			
	2589 (1)			V_4-4V_1
	2771 (1)			V_4-2V_1
			±2875 (10)	V_4-V_1
	2946 (6)		±2928 (10)	V_4
	3036 (1)		±2983 (10)	V_4+V_1
			± Due to ether	
(8VII)	(8VII)	—	—	References to other work.

computed differences on the assumed scheme in the next column; the last column of each table indicates the nature of the assumed combination or overtone. The fundamentals assumed behave so similarly in different compounds, that it is possible to number corresponding fundamental frequencies in different compounds with the same symbol; the symbols used are V_1, V_2, V_3, V_4. The way in which these fundamentals vary from group to group of compounds is regular and interesting. A fifth fundamental appears in the aromatic compounds.

The Raman spectrum of diethyl ether was studied, since Grignard compounds are prepared in ether solution; and for comparison with it, the Raman spectrum of ethyl alcohol was obtained. The wave-number shifts observed for ether are: 443 (1), 844 (2), 1159 (2), 1286 (2), 1466 (10), 2683 (2), 2793 (2), 2806 (5), 2873 (40), 2928 (30), 2983 (30) cm^{-1}. Nearly all these lines, except that at 2806, are broad. Other workers[7,8V,8VII,13]) list a few faint lines which we did not observe; but our list contains three lines not previously observed. Part of the difference may be due to wrong assignment of lines in the mercury arc spectra, and part may be due to the fact that our plates, while often underexposed, show the most-shifted Raman lines with greater relative intensity than reported by other workers. For alcohol, the observed shifts are: 1059 (3), 1108 (3), 1294 (3), 1461 (5), 2683 (1), 2880 (20), 2923 (20), 2976 (20). This list includes one new line, and fails to show one or two lines which are probably real, reported by other workers[7,8V,8VII,13,16]. The only regularity of structure to point out, is that in each case the last three lines can be represented by the formula $V_4 \pm V_1$, with $V_4 = 2928$, and $V_1 = 55$ cm^{-1} for ether and 47 cm^{-1} for alcohol. This regularity, while similar to that found in many other compounds, may prove to be illusory, as will be pointed out below.

In Table II are given the results from methyl bromide and methyl iodide, and from the Grignard reagents made from them. The plates were all underexposed, except for methyl iodide. Dadieu and Kohlrausch[8VII] have recorded

[16] Venkateswaran and Karl, Zeits. f. phys. Chem. **B1**, 466 (1928).

data on the first two of these compounds, including lines at 2956 and 3050 cm^{-1} for methyl bromide. No other work on the latter two compounds appears to have been published. The interesting result is the disappearance of the frequency marked V_3 in the table, and the appearance of a higher frequency, when the C-Br or C-I linkage changes to C-Mg-Br or C-Mg-I. This seems to indicate that the V_3 frequency is associated with the carbon-halogen bond. The group of frequencies around 3000 cm^{-1} is generally assumed to be associated with the C—H bond, since such lines always occur in both Raman and infrared spectra of compounds which possess this bond. In assigning the structure to these lines in the methyl iodide spectrum, a fundamental frequency at 88 cm^{-1} was assumed.

In the case of the mono-halogen derivatives of ethane, Table III, it is found possible to make every observed line on our plates fit into a scheme

TABLE III. *Raman spectra of ethyl halides.*

Ethyl chloride C_2H_5Cl		Ethyl bromide C_2H_5Br		Ethyl iodide C_2H_5I		Assumed combinations
Obs.	Comp.	Obs.	Comp.	Obs.	Comp.	
	41		48		53	V_1
	84		77		65	V_2
251 (1)	252					$3V_2$
341 (1)	336	308 (2)	308	261 (3)	260	$4V_2$
668 (10)	668	566 (15)	561		527	V_3
		968 (1)	978			$2V_3-2V_2$
1076 (1)	1084					$2V_3-3V_2$
1286 (1)	1295	1079 (1)	1084			$2V_3-V_1$
		1254 (5)	1255	1213 (6)	1213	$2V_3+3V_1$
		1456 (5)	1458			$3V_3-5V_1$
2716 (1)	2716					V_4-5V_1
2756 (1)	2757	2736 (1)	2731			V_4-4V_1
2866 (10)	2880	2875 (10)	2875			V_4-V_1
2921 (30)	2921	2923 (30)	2923	2915 (30)	2915	V_4
2961 (15)	2962	2976 (15)	2971	2968 (10)	2968	V_4+V_1
8V, 11		8V, 14, 11		8VII		References to other work

based on four fundamentals, the lower two being assumed but not observed. The plate for ethyl iodide was underexposed; this substance liberates iodine on exposure to light, and in spite of redistillation of the sample several times during the exposure, the absorption due to the iodine made the exposure time insufficient. This table is perhaps the most satisfactory of all those given.

The corresponding Grignard compounds gave no lines which could not have been attributed to the ether used as solvent. Moreover, most of these compounds are somewhat fluorescent; this difficulty prevented obtaining any other Raman spectra from Grignard reagents.

The results for dihalogen derivatives of ethane are given in the next two tables; Table IV deals with symmetrical derivatives, Table V with unsymmetrical derivatives. No other results appear to have been published on the latter group of compounds. The four-fundamental scheme works out similarly to the preceding cases, but less satisfactorily.

TABLE IV. *Raman spectra of symmetrical ethyl dihalides.*

Ethylene chloride $ClCH_2CH_2Cl$		Ethylene bromide $BrCH_2CH_2Br$		Assumed combination
Obs.	Comp.	Obs.	Comp.	
	44		52	V_1
	105		100	V_2
129 (1)	132			$3V_1$
		201 (5)	200	$2V_2$
311 (2)	315			$3V_2$
420 (1)	420			$4V_2$
658 (6)	654	558 (1)	563	V_3-V_2
759 (10)	759	663 (30)	663	V_3
1049 (1)				(?)
		1061 (4)	1063	V_3+4V_2
1211 (1)				(?)
		1264 (10)	1274	$2V_3-V_1$
1326 (2)				(?)
1451 (3)				(?)
2816 (1)	2829			V_4-3V_1
2866 (2)	2873	2874 (3)	2866	V_4-2V_1
2961 (30)	2961	2966 (30)	2970	V_4
3014 (3)	3005	3020 (8)	3022	V_4+V_1
8V, 14		8V, 14		References to other work

The results for tetrahalogen derivatives of ethane are given in Table VI. The spectra contain many lines, several of which do not fit well into the scheme of combinations assumed. The scheme seems forced and unconvincing, but it serves to point out interesting similarities with the Raman spectra of other compounds.

TABLE V. *Raman spectra of unsymmetrical ethyl dihalides.*

Ethylidene chloride CH_3CHCl_2		Ethylidene bromide CH_3CHBr_2		Assumed combination
Obs.	Comp.	Obs.	Comp.	
	60		55	V_1
	133	176 (1)	176	V_2
266 (2)	266	344 (1)	352	$2V_2$
401 (1)	399	551 (2)	528	$3V_2$
641 (10)	641	608 (2)	608	V_3
691 (1)	701			V_3+V_1
2946 (20)	2946	2921 (15)	2921	V_4
3006 (15)	3006	2976 (10)	2976	V_4+V_1

It is interesting to collect the values of the fundamentals used in the spectra of the various compounds described, as is done in Table VII. It will be seen that V_1 increases in frequency with increasing molecular weight (or increasing atomic weight of the halogen substituent) in all except the unsymmetrical compounds. The V_2 fundamental decreases with increase of molecular weight except in the unsymmetrical compounds, while V_3 decreases consistently in all the compounds. The V_4 fundamental is less variable, but it is thought that its variation can be explained better by an alternative method.

In addition to the foregoing data, results are here given for several compounds of cyclic structure. The plates for the first three do not show so many

TABLE VI. *Raman spectra of symmetrical ethyl tetrahalides.*

S-Tetrachloroethane $Cl_2HC \cdot CHCl_2$ Obs.	Comp.	S-Tetrabromoethane $Br_2HC \cdot CHBr_2$ Obs.	Comp.	Assumed combination
	50		73	V_1
	139		99	V_2
		121 (3)	120	$3V_1 - V_2$
101 (2)	100	156 (3)	146	$2V_1$
189 (2)	189	*186	172	$V_1 + V_2$
		*219 (10)	219	$3V_1$
248 (2)	250			$5V_1$
299 (2)	300			$6V_1$
359 (10)				(?)
558 (1)	550			$11V_1$
656 (8)	666			$V_3 - 3V_1$
		541 (3)		(?)
		628 (1)	617	$V_3 - V_2$
		666 (2)		(?)
816 (5)	816	716 (30)	716	V_3
		779 (2)		(?)
999 (4)	1005			$V_1 + V_2 + V_3$
1244 (3)	1233	1014 (5)	1013	$V_3 + 3V_2$
		1153 (5)	1140	$2V_3 - 4V_1$
		1206 (5)	1213	$2V_3 - 3V_1$
		2776 (2)	2777	$V_4 - 2V_1$
2931 (20)	2931	2923 (40)	2923	V_4
2996 (20)	2981	2996 (20)	2996	$V_4 + V_1$
8V, 10		8V		References to other work

*These frequencies apper as "antistokes" lines also.

lines as have been reported by other observers; they are probably underexposed. The results on these are simply listed here without any attempt to point out possible structure, beyond noting that the frequency at about 1000 cm^{-1} is apparently a new fundamental, V_5, and that the V_4 fundamental at

TABLE VII. *Collected values of fundamentals.*

	V_1	V_2	V_3	V_4	V_5
Diethyl ether $(C_2H_5)_2O$	55			2928	
Ethyl alcohol C_2H_5OH	47			2928	
Methyl bromide, CH_3Br			603		
Methyl iodide, CH_3I			534	2946	
Ethyl chloride, C_2H_5Cl	41	84	668	2921	
Ethyl bromide, C_2H_4Br	48	77	561	2923	
Ethyl iodide, C_2H_5I	53	65	527	2915	
Ethylene chloride, $ClCH_2CH_2Cl$	44	105	759	2961	
Ethylene bromide, $BrCH_2CH_2Br$	52	100	663	2966	
Ethylidene chloride, CH_3CHCl_2	60	133	641	2946	
Ethylidene bromide, CH_3CHBr_2	55	176	608	2921	
S-Tetrachloroethane, $Cl_2CHCHCl_2$	50	139	816	2931	
S-Tetrabromoethane, $Br_2CHCHBr_2$	73	99	716	2923	
Chlorobenzene, C_6H_5Cl	90	106	626	3076	1009
Bromobenzene, C_6H_5Br	75	104	606	3071	1006

about 3050 cm^{-1} has a somewhat higher frequency in the cyclic than in the aliphatic compounds.

Benzene, C_6H_6[8I, 8II, 8IV, 9, 7, 10, 11, 12]; 621 (1), 1003 (20), 1203 (3), 1619 (5), 3078 (50) cm^{-1}.

Pyridine, C_6H_5N[15, 13, 17]; 991 (10), 1033 (10), 1226 (3), 1586 (5), 3046 (50) cm^{-1}.

Benzyl chloride, $C_6H_5CH_2Cl$[8IV, 15]; 681 (1), 991 (3), 1601 (3), 2951 (3), 3046 (20) cm^{-1}.

In the case of chlorobenzene and bromobenzene, the kind of scheme of analysis attempted above succeeds rather better, all but one of the lines of each substance being representable as either a fundamental or as a combination line of some sort. The results are given in Table VIII.

TABLE VIII. *Raman spectra of phenyl halides.*

Chlorobenzene C_6H_5Cl		Bromobenzene C_6H_5Br		Assumed Combination
Obs.	Comp.	Obs.	Comp.	
	90		75	V_1
	106		104	V_2
		176 (3)	179	V_1+V_2
213 (3)	212			$2V_2$
316 (1)	318	313 (2)	312	$3V_2$
426 (3)	424			$4V_2$
626 (3)	626	608 (1)	606	V_3
716 (3)	716	678 (1)	681	V_3+V_1
789 (3)	787			V_5-2V_2
1011 (10)	1009	1006 (10)	1006	V_5
1098 (5)	1099	1073 (3)	1081	V_5+V_1
1183 (2)	1189	1171 (3)	1156	V_5+2V_1
		1586 (6)		(?)
2140 (1)	2148			$3V_2+3V_1$
2736 (1)				(?)
3076 (50)	3076	3071 (50)	3071	V_4
3188 (5)	3182			V_4+V_2
(8II, 10, 14)		(8II, 9, 14, 15)		

In attempting to discover some sort of system in Raman spectra, one should proceed with careful attention to the probable sources of error. These may be mentioned in three groups, in the present work. First, the data are too inaccurate to warrant any very great assurance that the apparent regularities found are significant. The wave-number shifts here reported were obtained with dispersion too small to yield exact values for the differences, and it is probable further that a number of the fainter lines were overlooked. The accuracy might be improved by using results from other observers, at least for the stronger lines; but on the other hand, the results reported from mercury arc excitation apparently contain so many spurious lines, due to the difficulty of deciding which of the various mercury lines really was the exciting line, that it seems clear that much of the work done using unfiltered mercury radiation will have to be repeated, in spite of the evident care with which

[15] Petrikaln and Hochberg, Zeits. f. phys. Chem. **B3**, 217 and 405 (1929); **B4**, 299 (1929).
[17] S. Venkateswaran, J. Phys. Chem. **34**, 145–152 (1930).

much of this work has been done. It is, of course, pointless to try to explain lines which in fact do not exist, just as it is discouraging to try to explain a spectrum from which the fainter lines are lacking.

Second, the lack of a theoretical basis for assuming the lower fundamentals used above is against the suggested scheme, as is the almost complete absence of these lower fundamentals. At first sight it might seem safe to assume fundamental frequencies so low in frequency as to be unobservable in the Raman spectra, and so low as to lie in the region of reststrahlen, so that infrared data would be lacking. But some of them at least are high enough in frequency so that they should not be covered up by the broad exciting line. Many of the combinations that would be expected from these fundamentals are not observed; and in a few cases, the intensities do not seem to fit in well. As will be pointed out below, most of such theory as is available seems to indicate that all the stronger Raman lines are fundamentals. On the other hand, overtones and combinations occur very frequently in infrared spectra; and in many Raman spectra the number of lines is so great that it seems impossible that all of them should be fundamentals. The absence of the lower frequencies is not a fatal objection; the reststrahlen frequencies of sodium chloride, for instance, do not appear in the Raman spectrum. But it will be interesting if liquids prove to have such low characteristic frequencies.

Third, it is frequently possible to find several ways of arranging a spectrum, which appear equally probable. If three frequencies A, B, and C, are found, such that $A+B=C$, it may be that C is a combination tone, or that either A or B is a difference-tone, or that the apparent relation is simply accidental. Again, it was found, for example, that all but four of the lines in the Raman spectrum of chlorobenzene could be set equal to integral multiples of a certain assumed fundamental. No reason could be given for the high intensity of some of the multiples and the absence of many of the others. Bromobenzene showed no analogous relation. Evidently the case was just another illusory relation. One more example may be pointed out; this is the case of carbon tetrachloride, which shows well the different ways in which a spectrum may be explained. On one hand, Langer[18] shows that the Raman frequencies of CCl_4 may all be explained as being due to *differences* between fundamental frequencies in the infrared spectrum, and even suggests a wave-mechanics theory to support the argument. On the other hand, Marvin[19] shows that the Raman frequencies of this compound can be explained, and the infrared spectrum as well, in terms of six fundamentals and their overtones and combinations; and the spectra of $SiCl_4$ are explained similarly. Next, Schaefer[20] shows that one of Marvin's fundamentals is unnecessary, as it is the octave of another; and by assuming that two of the remaining frequencies are a doublet, he is able to bring the whole scheme into good agreement with the theoretical results of Dennison[21] as necessarily modified to ap-

[18] R. Langer, Nature **123**, 345 (1929).
[19] H. H. Marvin, Phys. Rev. **33**, 952 (1929).
[20] C. Schaefer, Zeits. f. Physik **60**, 586 (1930).
[21] D. M. Dennison, Astrophys. J. **62**, 84 (1925).

ply to CCl_4 instead of to CH_4 (methane). The same is done for $SiCl_4$, and the possibility of similar treatment of $TiCl_4$ and $SnCl_4$ is pointed out, as well as certain similarities with compounds containing the SO_4 group. The arguments presented, and the manner in which the scheme fits the observed spectra, are extremely convincing, and there seems to be no reason to doubt the essential correctness of Schaefer's analysis. But if this is conceded, then it seems necessary to admit that overtone frequencies do appear in Raman spectra, as both Daure[7] and Pringsheim and Rosen[10] have observed Raman frequencies in the spectrum of CCl_4 which on Schaefer's scheme must be the overtone of one of the fundamentals.

In view of such facts, the writers do not present the suggested arrangements tabulated above as anything more than an interesting set of numerical approximations which it is hoped may be of use to some one in extending the theory of the Raman effect, as Marvin's suggested plan probably helped in analyzing the spectrum of CCl_4.

An attack on the problem from a quite different angle is made by Dadieu and Kohlrausch.[8] It is assumed that the chemical bonds in a molecule may be treated as a first approximation as if they behaved like elastic springs; so that when two atoms of masses m_1 and m_2 vibrate with respect to each other, the restoring force F is proportional to the displacement, x,

$$F = fx; \tag{1}$$

and the frequency of the oscillation is given by the equation

$$W_0 = 1/2\pi(f/\mu)^{1/2}, \tag{2}$$

in which μ, the "reduced mass" of the oscillating system, is given by

$$1/\mu = 1/m_1 + 1/m_2. \tag{3}$$

The theory has been extended to the case of anharmonic oscillations, and to the case of coupled vibrations, in which three bodies participate; but these parts of the theory are not immediately essential to the purpose of this paper. Dadieu and Kohlrausch have considered only longitudinal vibrations; but the case of transverse vibrations has been treated briefly in similar fashion by Andrews.[22] Following the theory outlined, the constant f is taken to be approximately proportional to the energy of dissociation A of the chemical bond between the vibrating atoms, this energy being known at least roughly from thermochemical data. Hence if one frequency due to a given pair of atoms is known, the frequency due to any other pair of atoms may be computed if the A's and the μ's are known. In this way, starting with the aromatic C-H frequency at 3050 cm^{-1} as a reference frequency, Dadieu and Kohlrausch have computed the frequencies to be expected from a large number of types of chemical bond, the computed values being usually somewhat lower than the observed values. In this way, and by comparison of similar compounds in a list of more than a hundred compounds studied, Dadieu and Kohlrausch have

[22] D. H. Andrews, Phys. Rev. **36**, 544 (1930).

been able to identify the characteristic frequencies of a considerable number of chemical bonds. The theory explains at once why in Raman spectra there is such a noticeable lack of lines between the C-H group, from 2850 cm^{-1} to 3100 cm^{-1}, and the lines due to the heavier atoms, most of which occur with shifts below 1700 cm^{-1}. The computations show that in cases where similar atoms are joined by single, double, and triple bonds, the average restoring forces are in the approximate ratio 1:2:3. As in infrared spectra, "internal" frequencies characteristic of vibrations within recurring groups, and "external" frequencies, associated with the vibrations of a group against the rest of the molecule, are distinguished. The theory checks with observation in so many ways that it seems impossible to doubt its essential correctness. Further evidence in this direction is afforded by the interesting experiments of Kettering, Shutts, and Andrews,[23] who constructed molecular models and, by noting resonance frequencies by stroboscopic methods when the models were vibrated, found sets of characteristic frequencies in good agreement with this theory.

So far as the theory has been applied to the compounds considered in the present article, frequencies for the carbon-halogen bonds are predicted which are in qualitative agreement with the frequencies marked V_3 in the tables; but no frequencies as low as the V_1 and V_2 assumed are predicted, and these may prove to be illusory. The V_4 frequency is clearly the C-H frequency; but if it is assumed that neighboring substituents can alter either the effective mass of the vibrating groups or the strength of the chemical bond between them, and Dadieu and Kohlrausch have presented abundant evidence that both these things occur, then it seems more probable that the occurrence of several lines in the C-H group is due to the existence of several modifications of the C-H bond in the molecules, rather than to combination with a hypothetical V_1 or V_2 frequency. The approximately equal frequency-differences observed are likely to prove not due to combinations. In all probability, more than four fundamentals will be required to explain the structure of most of the compounds discussed. This is especially likely to be true of the cyclic compounds. The fundamental V_5 is probably real, and characteristic of the benzene-ring structure. But Dadieu and Kohlrausch, Soderqvist,[11] and others have pointed out that there are three or four other frequencies which also seem to be characteristic of the ring structure. Whether these are all fundamentals, it is at present impossible to say. Dadieu and Kohlrausch have expressed the opinion that only fundamentals appear in Raman spectra; but an apparently valid exception to this statement has been pointed out above in the case of CCl_4.

It is hoped that further considerations may be presented in another paper in preparation by one of the writers.

[23] Kettering, Shutts, and Andrews, Phys. Rev. **36**, 531 (1930).

MODIFIED SCATTERING BY HYDROGEN HALIDES

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Abstract

Raman lines of the gases of HCl (previously measured by R. W. Wood), of HBr and HI and of the liquids of HCl and HBr have been measured. The Raman shifts of the lines of HCl and HBr gases agree with the infrared bands. The Raman shift of HI, 2233 cm^{-1}, does not agree with the infrared value and is considered the more accurate determination of the (0, 1) vibrational transition for HI. Intensities of scattering are in the reverse order of intensities of absorption, as might be expected from the Hill-Kemble theory of scattering by diatomic molecules of gases. The Raman lines scattered by the liquids show a different appearance from the lines scattered by the gases and their Raman shifts are smaller. The differences in the shifts are much too large to be attributed to a Lorentz-Lorenz force and are evidence of molecular interactions of a purely quantum mechanical nature, as discussed by Breit and Salant.

OF THE many measurements of modified lines scattered by liquids, usually by liquids of polyatomic molecules, few give unambiguous information about the energy levels of a molecule in both gaseous and liquid states. A notable exception is the work of McLennan and McLeod, which showed that the lower vibrational terms of O_2, N_2 and H_2 and the lower rotational terms of H_2 are sensibly the same in the two states.[1] This paper is concerned with Raman spectra of the gases and liquids of HCl, HBr and HI.

Raman lines, both vibrational and rotational, of the gas of HCl, had been measured already by Wood and by Wood and Dieke.[2] The modified lines of the gases of HBr and HI have been reported briefly by us.[3] Early measurements of the modified line of liquid HCl, first by us [4a] and then by Daure,[4b] are superseded by our later, more accurate determinations, which included also the modified line of liquid HBr.[4c]

Apparatus and Experimental Procedure

The Hilger constant deviation glass spectrograph was used, with the large camera for the liquids and both large and small camera for the gases. The dispersions on the plate in the region λ4600 were 118 cm^{-1} per mm for the large camera, 344 cm^{-1} per mm for the small, the latter being very much the faster of the two systems, of course. The plates were calibrated by iron arc standards. Incident radiation was from mercury arcs.

[1] J. C. McLennan and H. J. McLeod, Nature **123**, 160 (1929).
[2] R. W. Wood, Phil. Mag. **7**, 744 (1929); R. W. Wood and G. H. Dieke, Phys. Rev. **35**, 1355 (1930).
[3] E. O. Salant and A. Sandow, Phys. Rev. **36**, 1591 (1930).
[4] (b) P. Daure, Trans. Far. Soc. **25**, 825 (1929). E. O. Salant and A. Sandow, (a) Science **69**, 357 (1929), (c) Phys. Rev. **35**, 214 (1930).

With the gases, we employed the method developed by R. W. Wood,[1] a long diaphragmed tube containing gas at atmospheric pressure and a long arc alongside it, both tube and arc being surrounded by polished aluminum reflectors. For HCl and HBr we used a glass tube 2 inches by 50 inches and a 50-inch glass arc. With HI (and also HBr) we used a 20-inch quartz arc and a 20-inch glass tube, the latter having an outer shell containing a solution of quinine sulphate to absorb the short wave radiation which decomposes HI.

The cells for the liquids were the usual, small cylindrical tubes into which was focussed the incident radiation from a 6-inch quartz arc. The cell was placed inside an unsilvered Dewar flask containing enough liquid air to liquefy the gas and keep it about 5°C below the boiling point as it was distilled

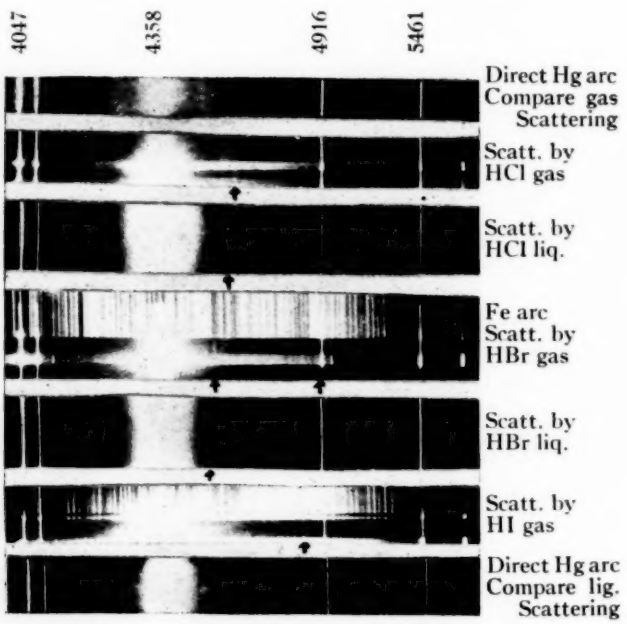

Fig. 1. Spectrograms of scattering by hydrogen halides.

into the cell. Even with filters we were unable to prevent the formation of iodine sufficiently to obtain modified lines from liquid HI.

HCl was prepared by dropping H_2SO_4 on NaCl in HCl solution. HBr and HI were prepared by the action of boiled-down syrupy phosphoric acid on NaBr and NaI. The gases were dried by passing them through suitable chemical reagents (H_2SO_4 for HCl, P_2O_5 for the others) and through cooled traps. The whole system, generator-driers-cell, contained only quartz and Pyrex fused or ground joints, including no rubber tubing nor cements in the path of the gases.

In spite of the drying of the gases and of the cells, the gases all appeared misty at first, the mistiness disappearing after a few hours; this had already been noticed by Wood with HCl[2]. Spectrograms were begun only after the substances were clear.

Results

After exposures of from 19 to 72 hours with the gases and 2 to 7 hours with the liquids, modified lines could be clearly distinguished on the plates. Spectrograms are shown in Fig. 1, and microphotometer curves in Fig. 2. Lines from HCl were scattered from the mercury line λ4047, lines from HBr from 4047 and 4358, and lines from HI from 4358, all Stokes lines.

The microphotometer curves were not at all clear, because of continuous background and because of the small deflections resulting from the short slits used in the spectrograms. Consequently, features of the modified lines were

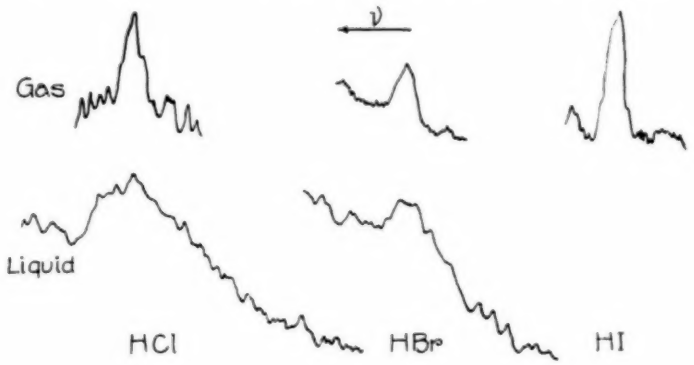

Fig. 2. Microphotometer curves of shifted lines.

much more obvious to the eye; for example, the long-wave edges of the modified lines of all the gases appear sharper than their short-wave edges, whereas the reverse is true of the modified lines of the liquids. The comparative sharpness of the long-wave edge can be seen in the microphotometer curve of HI. The greater diffuseness of the long-wave edges of the lines of the liquids of HCl and HBr, and the greater sharpness of the gas lines as compared with the lines of the liquids can also be seen even from these curves.

For the evaluation of the Raman shifts we took 24,705.4 cm^{-1} for λ4047; 22,938 cm^{-1} for λ4358.

Table I. *Raman shifts, gases.*

	ν_L	ν_D	ν_S	Intensity
HCl	2885.5	2879	2867	Least
HBr	2558	2550	2524	
HI	2233	2216	2201	Greatest

Table II. *Raman shifts, liquids.*

	ν_L	ν_D	ν_S	Intensity
HCl	2800	2770	2756	Least
HBr	2487	2466	2455	Greatest

The measurements of the modified lines of the gases are in Table I, of the liquids in Table II. In the second column are the Raman shifts of the long-wave edge of the modified line ν_L, in the third column the shifts of the most intense point of the modified line ν_D, in the fourth column the shifts of the short-wave edge ν_S, and in the last column is the order of intensities. All values are in cm^{-1}.

The most striking difference between the modified lines of the gases and of the liquids is that the latter are displaced to smaller frequencies as compared with the corresponding gases; this will be discussed below. It is to be noted further that the points of maximum intensity of the gases of HCl and HBr are nearer the long than the short wave edge, whereas the reverse is true for the liquids of HCl and HBr.

Discussion

The modified lines of the gases are, obviously, Q branches corresponding to jumps of the vibrational quantum number $\Delta v = 1$ and the frequency shifts ν_L of the long wave edges of the gas lines measure the vibrational change $\Delta G(\frac{1}{2})$, (Mulliken's notation[5]).

That this is true for HCl has already been shown by Wood,[2] our value 2885.5 ± 0.5 cm^{-1} being in good agreement with his, 2886.0.

Similarly, our value 2558 ± 2 cm^{-1} agrees within the limits of experimental error with the center of the $(1 \leftarrow 0)$ vibration-rotation band of HBr, 2559.1, determined by Randall and Imes.[6]

Quite the contrary is the case for HI. Because of its weakness and its proximity to a strong atmospheric band of CO_2, no really accurate measurement of the fundamental absorption band exists. In spite of these difficulties, Czerny[7] succeeded in detecting a weak doublet which seemed to indicate the band center at about 2270 cm^{-1}. Our value 2233 ± 2 cm^{-1} differs from this certainly beyond any apparent experimental error and, since the uncertainties of the absorption experiments do not adhere to these light-scattering experiments, must stand for the present as the value of $\Delta G(\frac{1}{2})$ for HI.

The intensities of scattering of the modified lines are in the order HI > HBr > HCl, just the reverse of the intensities of absorption of the corresponding infrared bands. The electronic levels of these molecules nearest the exciting lines of these experiments are the levels for the ultraviolet continuous bands whose long wave heads are: HCl 45455, HBr 37879, HI 30120 cm^{-1}.[8,9] The differences, then, between these heads and our exciting lines are in the order HI < HBr < HCl. Now, according to the theory of intensities of modified scattering, discussed in particular for diatomic gaseous molecules by Hill and Kemble,[10] these differences would appear in the denominator of the ex-

[5] R. S. Mulliken, Phys. Rev. **36,** 611 (1930).
[6] H. M. Randall and E. S. Imes, Phys. Rev. **15,** 152 (1919).
[7] M. Czerny, Zeits. f. Physik **44,** 235 (1927).
[8] H. C. Tingey and R. H. Gerke, J. Am. Chem. Soc. **48,** 1838 (1926).
[9] Coehn and Stuckardt, Zeits. f. physik. Chem. **91,** 722 (1916).
[10] E. L. Hill and E. C. Kemble, Proc. Nat. Acad. Sci. **15,** 387 (1929).

pression for the electric moment associated with the Raman line, and should contribute, then, toward effecting just the order of intensities observed here.

With the liquids, it is not certain, as with the gases, that the shift of the long wave edge of the Raman line measures the change $\Delta G(\frac{1}{2})$ of the molecules. First there is the fact that absorption measurements of the (0, 2) bands of the liquefied hydrogen halide molecules have shown the bands to have no apparent structure but to have a single maximum of absorption;[11] one can hardly speak of these bands having P, Q and R branches, consequently. Then the distribution of intensity in the modified lines from the liquids is different from that in the gases, as noted above, and their shapes seem to correspond to the shapes of the single infra-red bands. As in these bands it is the maximum that is taken as the measure of the vibrational change, it seems reasonable to take the shift of the point of maximum intensity, ν_D, of the liquid Raman lines as a measure of $\Delta G(\frac{1}{2})$ of the liquefied molecules. (Grating measurements of the $(1 \leftarrow 0)$ bands in the infrared are now in progress in these laboratories to determine this point).

Defining the change in vibrational term differences due to liquefaction as $\Delta_l \Delta G = \Delta G - \Delta G_l$ where ΔG_l refers to the value of ΔG in the liquids, we have in Table 3 the various values of $\Delta_l G(\frac{1}{2})$ depending on whether the long wave edge or the point of maximum intensity of the liquid lines is taken as a measure of $\Delta G_l(\frac{1}{2})$.

TABLE III. *Gas-liquid shifts of 0,1 transition.*

	Values of $\Delta_l \Delta G(\frac{1}{2})$	
	From ν_L	From ν_D
HCl	86	116
HBr	71	92

The theory of shifts of frequency accompanying close packing of molecules attributes the shifts ($\Delta_l \Delta G(\frac{1}{2})$ in these experiments) to three effects (1) electrostatic interaction of a molecule with its neighbors due to its excitation, (2) the effect of the finite space extension of the eigenfunctions of neighboring molecules and (3) the Lorentz-Lorenz force with effective charge replacing classical charge.[12] It was shown in that work that the frequency displacement accompanying liquefaction of HCl was only about 2.2 cm^{-1} due to the Lorentz-Lorenz effect. Since the other factors in the expression for the Lorentz-Lorenz shift are about the same for HBr as for HCl, and since the effective charge for HBr is smaller, corresponding to its smaller intensity of absorption, the Lorentz-Lorenz shift for HBr is of the order of 2 cm^{-1} and, as for HCl quite small compared to the displacement $\Delta_l \Delta G(\frac{1}{2})$ observed here and recorded in Table III. These displacements must, then, be attributed to the first two, purely quantum mechanical effects.

Gas-liquid frequency difference of the same order of magnitude as these have been reported for other substances; for example, for NH_3 by Dickinson,

[11] E. O. Salant and W. West, Bulletin Phys. Soc. **5**, 15 (Nov. 15, 1930).
[12] G. Breit and E. O. Salant, Phys. Rev. **36**, 871 (1930).

Dillon and Rasetti[13] and by Daure,[14] and for H_2S by Bhagavantam.[15] It is tempting to speak of these, too, as a quantum mechanical effect, but in the absence of further information about these molecules, in particular about their effective charges, such a conclusion would be premature and open to question.

We take great pleasure in thanking Mr. R. L. Garman of the Chemistry Department of Washington Square College for the microphotometer curves, and the General Electric Vapor Lamp Co. for mercury arcs. This research was begun while one of us (E.O.S.) was a Fellow of the National Research Council.

[13] R. G. Dickinson, R. T. Dillon and F. Rasetti, Phys. Rev. **34,** 582 (1929).
[14] P. Daure, Comptes rendus **188,** 61 (1929).
[15] S. Bhagavantam, Nature **126,** 502 (1930).

IONIZATION OF ARGON, NEON AND HELIUM BY VARIOUS ALKALI IONS

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(Received January 5, 1931)

Abstract

Caesium, rubidium, potassium, and sodium positive ions from Kunsman catalyst sources, and lithium ions from spodumene have been used to produce ionization in helium, neon, and argon. In most cases the ionization sets in between 100–150 volts and increases linearly to 750 volts, the highest potential used. Maximum ionization was produced in each gas by the alkali ion closest to it in atomic number.

PREVIOUS experiments have been reported[1] concerning the ionization of various gases by potassium positive ions of relatively low energies. The present paper deals with the ionization of helium, neon, and argon by a series of alkali ions representing a wide range of atomic weights from lithium to caesium. It was of interest to determine what relationship might exist be-

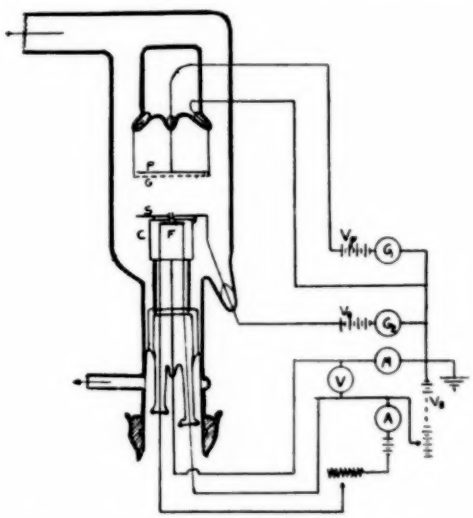

Fig. 1. Experimental tube and connections.

tween the various ionizing agents and the ionization which they produce in gases of different atomic weights. Some rather unexpected experimental results came to light which indicate that the field is fruitful for further investigation and explanation.

The method of measurement has been described in the previous papers. Referring to Fig. 1, it may be summarized briefly as follows. Positive ions

[1] R. M. Sutton, Phys. Rev. **33,** 364 (1929); Sutton and Mouzon, **35,** 694 (1930).

emitted from Kunsman catalyst sources by a hot coated platinum strip F are directed by the variable accelerating potential, V_a, through a small channel in the steel cathode C which completely surrounds the filament. Any ionization occurring in the gas between C and the grid G will produce an electron current I_s to the collector plate S which is connected to the high sensitivity galvanometer G_2. The initial positive beam (except for loss by scattering and the small fraction striking the grid) falls upon the upper plate P and is recorded as a positive ion current, I_p, by the galvanometer G_1. At each gas pressure used, the accelerating potential of the positive ions is varied in steps from zero to 750 volts. The ratio of currents, I_s^-/I_p^+, corrected for the small secondary emission of electrons from the grid, is taken as a measure of the ionization produced in the gas between S and G. The collector S and plate P are both maintained at small positive potentials to prevent the escape of elec-

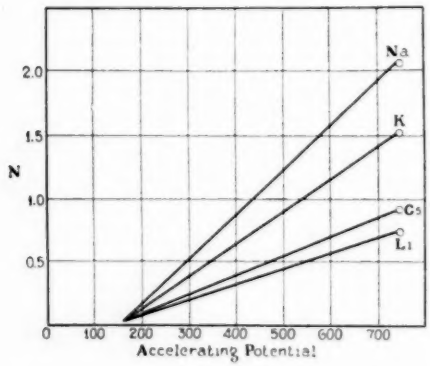

Fig. 2. N, number of neon ions formed per initial positive ion per cm path at 1 mm pressure.

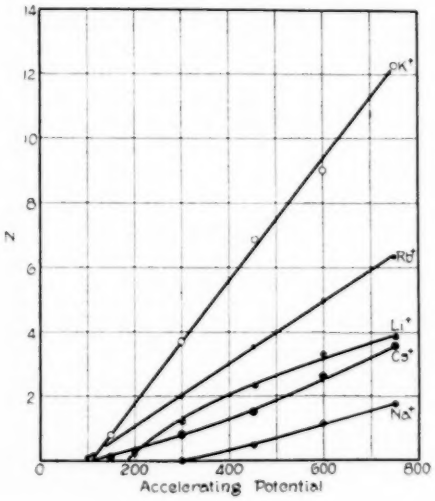

Fig. 3. N for argon.

trons due to secondary emission or photoelectric effect. These potentials were in no case high enough to produce ionization of the gas by electron collision. The distance $S-G$ (2.5 cm) is made large in comparison with the distance $G-P$ (0.2 cm) in order to minimize the effect of ionization between grid and plate. To correlate the results obtained at different pressures, the ratios of I_s/I_p were divided by the length of path between S and G and by the gas pressure in mm of mercury, thus giving the number, N, of ions formed per initial positive ion per centimeter path at one millimeter pressure. The pressure range utilized was from 0.005 to 0.05 mm; in a few cases where the ionization was feeble, pressures as high as 0.1 mm were used.

In general the ionization sets in between 100 and 150 volts (except for sodium in argon) and increases practically linearly with increasing accelerating potential to 750 volts, the highest voltage used. After making correction for the stoppage of the initial positive beam by the gas, the ionization for a particular voltage is found to be linear with respect to pressure; only in the

cases of intense ionization is there evidence of more than one ionizing collision per positive ion at the higher pressures and accelerating potentials. Thus N for each positive ion in a particular gas is independent of gas pressure within the range studied and depends only upon the accelerating potential of the positive ions.

Fig. 2 and Fig. 3 show the results of a large number of runs in neon and argon respectively, in each of which several different positive ions were used as the ionizing agents. The calculated values of N are seen to be practically linear with accelerating potential after ionization once begins, in most cases by 150 volts. Sodium does not ionize argon until an accelerating potential of nearly 300 volts is reached; this behavior, together with a strong reflection of the sodium positive ions to the collector S at accelerating potentials around 150–250 volts, is strangely unaccountable. In all other cases, reflection of the

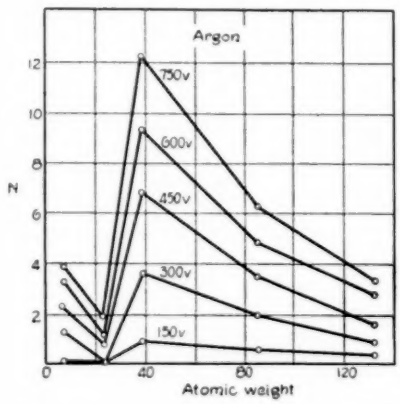

Fig. 4. N as function of atomic weight of positive ions and their energies.

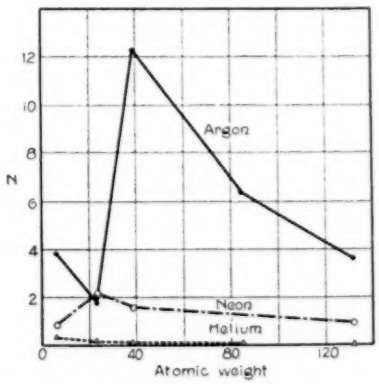

Fig. 5. Comparative values of ionization at 750 volts accelerating potential for different gases as function of atomic weight of ionizing agent.

positives played a negligible part in the currents observed. This method is not sensitive enough to determine the onset of ionization closer than 25 volts, but the slopes of all the ionization curves indicate a fairly sharp origin of ionization which was scarcely to be expected; the "ionization potential" due to positive ions bears no evident relationship to ionization potentials determined by electron impact methods, nor does it seem to be critically dependent upon the mass of the bombarding ions in any regular fashion.

The most striking results of this investigation appear when the values of N in Fig. 3 are plotted against atomic weight of the ionizing agent, as shown in Fig. 4. It appears that the maximum ionization in argon is produced by potassium positive ions, which is scarcely what would be expected from any ballistic transfer of energy considerations. Similarly, as may be seen in Fig. 5, neon is most strongly ionized by sodium positives; helium is most strongly ionized by lithium. The conclusion presents itself that *ionization of a noble gas is best effected by that alkali ion closest to it in mass or number of electrons.* Evidence is not yet available to discern whether the controlling factor is one

of mass or electron configuration of the two constituents of an impact, nor can a comparison yet be made with the ionization of a gas by its own atoms or ions. The experimental difficulties in the path of this latter aspect of the problem have not been solved.

Similar results have been published recently by Dr. Otto Beeck[2] who secured homogeneous beams of positive ions by means of a magnetic analyzer. His method is evidently better designed for the purpose than the one here reported, and he is now in a position to complete the study of the two remaining noble gases at this Institute. The qualitative agreement between the two methods is excellent, and the quantitative agreement is as good as might be expected considering the difference in methods. The only marked departure from regularity of our results appears in the relative interchange of intensities of ionization by lithium and sodium in argon. This may be accounted for by either or both of two causes: first, an impurity of higher atomic weight in the lithium source derived from powdered spodumene (all other sources were Kunsman catalysts); second, the unaccountably large reflection of sodium ions by argon. This inversion of position was carefully checked, and as far as the accuracy of this method is concerned, the effect is real.

Not only is there maximum ionization produced by the alkali positive lying closest to the atomic weight of the gas bombarded, but the intensity of these maxima increases greatly in the heavier gases. The ionization of helium is very feeble, whereas in argon it is quite pronounced. It is rather to be expected that even greater ionization will be found in xenon and krypton. In all of the foregoing work, correction has been made for the secondary emission of electrons from the metal parts of the tube. Inasmuch as there was gas admitted into the tube, no particular precautions were taken to outgas the electrodes. Comparing the secondary emission of the metal surfaces under bombardment of the various alkali ions, the intensity of emission was found to vary in the same way as the intensity of ionization; i.e., greatest for potassium when argon had been present, etc. It would appear that the secondary emission might be due largely to a layer of gas upon the electrodes, and hence this surface effect would bear a close relationship to the volume ionization produced in the gas by different positive ions.

It is felt that more experimental evidence is necessary before an adequate explanation of ionization by two such complicated structures as an alkali ion and a gas atom can be made. This necessitates the development of additional ion sources and improved technique for the study of atom-beams in a gas.

The authors acknowledge their thanks to Dr. Otto Beeck and Dr. Fritz Zwicky for stimulating discussion of the results obtained.

[2] Otto Beeck, Ann. d. Physik **6**, 1001 (1930).

A DIRECT MEASUREMENT OF MOLECULAR VELOCITIES

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University of California, Berkeley

(Received January 7, 1931)

Abstract

A method is described for the direct measurement of the velocities of neutral molecules. The molecules condense on a glass plate fastened to a cylinder which rotates at a high speed, 241 r.p.s. The molecules having velocities from 168 m/sec to 673 m/sec were spread over a band 3 cm wide. A stream of bismuth molecules is studied and the vapor found to be composed of 40 percent Bi and 60 percent Bi_2 at a temperature of 851°C.

Introduction

ONE of the fundamental assumptions of the kinetic theory of gases is the continual heat motion of the molecules in the gas. Even though there was no direct experimental verification of this assumption, the theoretical development progressed rapidly, resulting in the derivation of an expression for the distribution of molecular velocities by Maxwell[1] in 1859 and, later by Boltzmann.[2] This law has found many applications and until 1920 was only indirectly verified.

The first attempt at a direct measurement of molecular velocities was made by Stern[3] who intercepted a stream of silver atoms on a rotating plate. The displacement obtained was not sufficient to allow an analysis of the deposit beyond the location of the maximum. The results for the maximum agreed within the experimental error, about 15 percent, with that calculated from the theory. In 1927 Costa, Smyth, and Compton,[4] using rotating radially slotted disks and a radiometer vane as a detector attempted to secure a "velocity spectrum" of neutral molecules. Their results were in general qualitative agreement with the Maxwell-Boltzmann law but rather unsatisfactory because of the insensitivity of the detector. Eldridge,[5] using rotating disks as a velocity selector and condensing the molecules on a liquid-air cooled target, obtained a density distribution for cadmium which agreed fairly well with the theoretical distribution. Several objections might be raised, for his zero mark is not sharply defined but very broad; the zero of the theoretical curve has to be shifted about 0.05 cm to make the maximum of the theoretical curve coincide with the maximum of the deposit; his temperature measurement is unsatisfactory and his resolution is low. Lammert[6] developed a method for

[1] J. C. Maxwell, "Collected Works," **1,** 378 (1860) Cambridge University Press, Cambridge.

[2] L. Boltzmann, "Vorlesungen über die Gas Theorie," **1,** 15 (1910). Johann Barth, Leipzig.

[3] O. Stern, Zeits. f. Physik **2,** 49 (1920); **3,** 417 (1920).

[4] Costa, Smyth, and Compton, Phys. Rev. **30,** 349 (1927).

[5] J. A. Eldridge, Phys. Rev. **30,** 931 (1927).

[6] Berthold Lammert, Zeits. f. Physik **56,** 244 (1929).

producing molecular beams containing well-defined velocity bands. By taking a series of runs in which the bands had a definite width of 50 m/sec over a range of from 90 to 360 m/sec and determining the intensity of each band, a test of the Maxwell-Boltzmann law for mercury vapor was possible. Except for a systematic difference the results agree quite well with the theoretically expected distribution.

Theory

The aim of this experiment is to develop an apparatus with a resolving power greater than that obtained by Stern and Eldridge and thus allow a more detailed study of the "velocity spectrum" of neutral molecules. This, as shown later, can be attained by increasing the path-length and the speed of rotation.

Consider a gas issuing through a rectangular slit, g_1 (Fig. 1) in a side of the enclosure E which can be maintained at a constant temperature T. Let Knudsen's[7] condition for molecular streaming be satisfied, i.e., let the temperature be so controlled that the mean free path of the molecules within, is greater than the width of the slit g_1. With the aid of the slit g_2 a sharply defined rectangular beam is formed. Let a cylinder D, having a slit g_3 in its periphery and capable of being rotated, be placed in the path of this beam. If the cylinder is at rest, and slit g_3 is in the path of the molecular beam, a deposit forms on the rim at P diametrically opposite the slit. If the cylinder is rotated, the molecules entering g_3 require a finite time to traverse the diameter and consequently strike the rim at a point s to the left of P. The displacement s of a molecule moving with a speed c is given by the equation

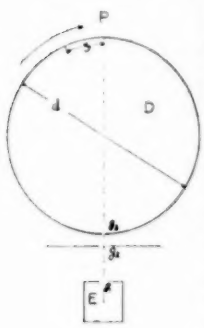

Fig. 1.

$$s = \pi d^2 n/c = A/c \tag{1}$$

where d is the diameter of the cylinder and n is the number of revolutions per second. The equation also shows that, by making d and n large, one may secure large displacements of the molecules, i.e., high resolving power.

The molecules in the beam possess not one definite velocity, but a distribution of velocities and consequently a "velocity spectrum" is formed on the rim of the cylinder. The density of this deposit should bear some relation to the velocity distribution in the enclosure E. According to the Maxwell-Boltzmann distribution law, the number of molecules dn out of a total number N in equilibrium within the enclosure possessing speeds between c and $c+dc$, is given by the expression

$$dn = \frac{4N}{\alpha^3 \pi^{1/2}} e^{-c^2/\alpha^2} c^2 dc$$

where α is the most probable speed of the molecules within the enclosure. As

[7] M. Knudsen, Ann. Physik **28**, 999 (1909).

shown by Stern,[3] while the molecules within the enclosure are in equilibrium those in the beam are not, for the number passing through the slit per second depends on the size of the opening, the shape of the enclosure, the speed of the molecules and the number of molecules in the enclosure. Let dn_1 be the number of molecules out of N_1 molecules in the beam possessing speeds between c and $c+dc$. Then

$$dn_1 = dn \cdot c \cdot K$$

where K is a constant. From this we get

$$dn_1 = (2N_1/\alpha^4)e^{-c^2/\alpha^2}c^3dc \tag{2}$$

as the expression for the velocity distribution in the beam.

To find the expression for the distribution of the molecules on the receiving plate, P, one can use the method given by Stern.[8] Consider first that the undeflected image is of infinitesimal width and find the distribution of the molecules in the deflected portion of the plate. Consider the velocity range between c and $c+dc$ giving a deflected range between s and $s-ds$. The intensity of the beam in the deflected region may be defined as the number of molecules dn striking and condensing on a length of plate ds assuming the beam to be of uniform and constant intensity across the element of length, or

$$I = dn/ds. \tag{3}$$

From Eqs. (1), (2), and (3) we get

$$I = \frac{2N_1}{\alpha^4 A}e^{-c^2/\alpha^2}c^5. \tag{4}$$

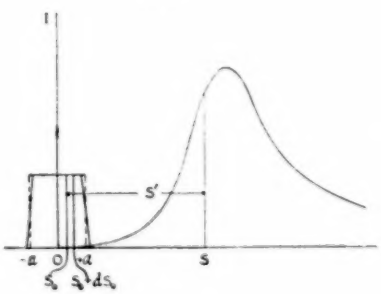

Fig. 2.

The undeflected beam in the actual experiment is of finite width 2a (Fig. 2). Let ds_0 be an element of length in the undeflected region and let dn_0 be the number of molecules striking and condensing on ds_0. Then $I_0 = dn_0/ds_0$. For an undeflected beam of width ds_0, Eq. (4) becomes

$$I = \frac{2I_0 ds_0}{\alpha^4 A}e^{-c^2/\alpha^2}c^5. \tag{6}$$

It will be more convenient to use the intensity distribution in the deflected portion as a function of the distance s from the zero line. Then $c/\alpha = s_a/s$,

[8] O. Stern, Zeits. f. Physik **41**, 563 (1927).

where s_α is the deflection of the molecules having the most probable velocity in the enclosure, and Eq. (6) becomes

$$I = \frac{2I_0 ds_0}{s_\alpha}\left(\frac{s_\alpha}{s}\right)^5 e^{-(s_\alpha/s)^2}. \tag{7}$$

Integrating (7) from $-a$ to $+a$, we get

$$I = I_0\left\{e^{-(s_\alpha/s+a)^2}\left[\left(\frac{s_\alpha}{s+a}\right)^2 + 1\right] - e^{-(s_\alpha/s-a)^2}\left[\left(\frac{s_\alpha}{s-a}\right)^2 + 1\right]\right\} \tag{8}$$

as the theoretical intensity distribution in the deflected region of the plate in terms of s_α and a.

Apparatus

The substance whose velocity distribution is to be determined is vaporized in a steel crucible A (Fig. 3). The vapor then passes through the channel in

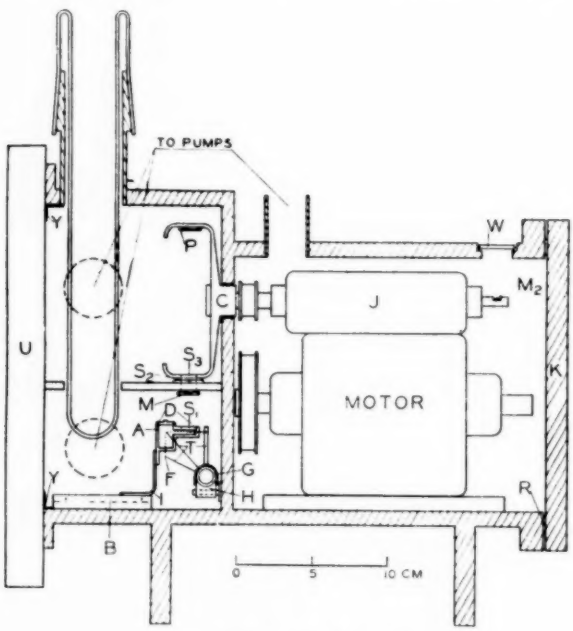

Fig. 3. Diagram of apparatus.

the neck to the slit S_1, there escaping as a molecular beam. The crucible is fastened to the sliding base B by means of a rectangular strip of invar I. This sliding base is fitted into a dove-tailed groove in order that the entire crucible and slit assembly can be easily removed for filling purposes and then replaced without changing the alignment of the slit system. Directly above the neck of the crucible is a second slit S_2 used to define sharply the molecular beam. The crucible slit is 0.05 mm by 10 mm in size while the defining slit is 0.6 mm by 10 mm. The distance between these slits is 3.29 cm. A shutter M magnetically operated from the outside is used to interrupt the beam.

The crucible is heated by radiation from a 300 watt tungsten lamp filament F mounted with the aid of tungsten supports T fused to a glass tube G. The glass tube is fastened in a special holder H allowing the filament to be adjusted in any desired direction. The loss of heat by radiation is reduced by surrounding the crucible and filament assembly with nickel radiation shields. Two chromel-alumel thermocouples fastened at D serve as a means of determining the temperature. The thermocouples are calibrated by comparison with a standardized platinum-platinum rhodium thermocouple. A potentiometer is used to read the electromotive force of the thermocouples.

A cylinder C, 10 cm in diameter, machined out of a solid piece of machine steel, is placed above the slit system. This cylinder is designed to withstand the forces due to high speeds of rotation with the least possible deformation. A knife edge slit S_3, 0.6 mm wide, is cut into the rim of the cylinder. Directly opposite on the inner rim a device is fastened to hold a curved glass plate P. The cylinder is carefully balanced and mounted on the high speed spindle J of an internal grinder. Its speed is determined by the stroboscopic method.

The grinder consists of a 1/6 H.P. universal motor and a high speed spindle mounted on top of the motor housing. A fabric belt is used to drive the spindle. The motor armature has a speed of 10,000 r.p.m. and the spindle 30,000 r.p.m. when connected to a 110-volt circuit. The armature and spindle rotate in ball bearings and the entire assembly is so well-balanced that vibration is negligible at nearly all speeds. The bearings are properly lubricated by vacuum pump oil which has been boiled in a vacuum for several hours to drive off the more volatile products. The residue is sufficiently non-volatile so that a pressure of less than 10^{-4} mm of mercury can easily be maintained in the motor compartment by continual pumping.

The entire assembly is enclosed in a phosphor-bronze housing which is divided into three compartments, a motor, a cylinder, and a crucible compartment. A hole in the wall between the motor and cylinder compartments, slightly larger than the hub of the cylinder, allows the high speed spindle to pass through and at the same time prevents the passage of large quantities of vapor from the motor to the cylinder compartment. A water jacket surrounds the outside of that portion of the housing subjected to heating. The end of the motor compartment is flanged and can be closed by bolting a metal plate K to this flange. A rubber gasket R is placed between the flange and plate to render the joint vacuum tight. The flange surrounding the cylinder and crucible compartments is scraped to fit a plate glass cover U. The joint between the glass cover and the flange is made vacuum tight by giving it a thin uniform coating of a special stopcock grease to which more pure rubber and paraffin has been added than is customary.

The entire system is evacuated through an opening in each compartment. All openings and tubing are large in diameter and the tubing is kept as short as possible in order that all vapors can be quickly removed. Three mercury vapor pumps each backed by a Hyvac pump are used to evacuate the compartments. Liquid air traps are used to prevent the mercury vapor from diffusing into the system. A glass tube which can be filled with liquid air passes

vertically through the cylinder chamber into the crucible chamber. A vacuum tight joint is made by the ground-glass, metal joint at the top. Copper shields *Y* are fitted into the corners formed by the glass cover and the sides, top and bottom of the housing. Copper strips attached to these shields are fastened to the glass tube. The liquid air in the tube cooled these shields to a sufficiently low temperature to condense most of the vapors from the stopcock grease. The tube itself also acts as a large cooled surface which condenses all condensible vapors coming in contact with it. No difficulty is experienced in maintaining a pressure of less than 10^{-5} mm of mercury in the crucible and cylinder compartments.

In order that the density of the deposit can be measured by a microphotometer it is desirable to use glass plates as receivers. These plates (6 by 1.5 by 0.03 cm) are cut from microscope cover glasses. They are bent so as to fit the inner circumference of the cylinder by balancing them on a carbon block having the proper curvature, and then placing the block in an electric oven. The temperature is raised slowly until the plate bends under its own weight to the shape of the carbon form.

For the bismuth molecules to condense on the glass plate at room temperature it is necessary to place an initial, thin and uniform layer of bismuth upon it. This is accomplished by a piece of apparatus which allows the glass plate to be cooled to near the temperature of liquid air and then uniformly exposed to a stream of bismuth molecules. This apparatus consists of an electrically heated crucible and a glass liquid air container mounted in a brass housing which can be made vacuum tight and evacuated. The glass plate upon which the initial deposit is placed is held against the curved flat bottom of the liquid air container by two flat springs. The crucible containing the substance to be deposited is mounted on a shaft so that it may be rotated from one side of the plate to the other. This rotation is accomplished from the outside of the housing by fastening a bent arm to the shaft and enclosing the arm within a sylphon. A fork, attached to a motor-driven slow-speed gear, engages the sylphon thus transmitting the motion to the crucible.

Experimental Procedure

The bismuth used in this experiment is the analyzed product of Powers-Weightman-Rosengarten Company, Philadelphia. In order to get rid of any adsorbed gases it is heated in a vacuum to a temperature of 450°C for about five hours and then allowed to cool before air is admitted.

A bent glass plate is thoroughly cleaned and dried, then placed in the "initial depositing" apparatus and given a thin uniform coating of bismuth. The plate is fastened to the cylinder. The cylinder is adjusted with the aid of a traveling microscope until the slit S_3 is observed to be directly above the defining slit S_2. It is then fixed in this position. The system is evacuated, the crucible heated to about 800°C and the plate exposed to the molecular beam for about 20 seconds. This operation gives a visible deposit on the plate and forms the zero mark from which the displacements are measured. After ad-

mitting air to the system, the plate is removed and a microphotometer record obtained of the density of the initial deposit and location of the zero mark.

The plate is again fastened to the cylinder, the crucible filled with bismuth and the system evacuated. A slow increase in the temperature is necessary to avoid the violent expansion of gas bubbles in the molten metal which results in a "spitting" of the metal through the slit. When the temperature of the furnace reaches equilibrium and the motor speed is adjusted by varying the resistance in the line to the absence of beats, the shutter is opened and the beam allowed to pass to the plate. The maximum of the deposit first becomes visible in from three to six hours depending upon the temperature and speed of the run. The run is continued for periods ranging from eight to twenty-two hours. The plate is removed from the cylinder and again photometered. Finally, the two photometer curves are superimposed and the density due to the velocity distribution is measured.

Results

The results of four runs are given. Runs 1 and 2 are represented with their theoretical curves in Fig. 4. Fig. 5 is a contact print of the photometer record from which the data for curve 1, Fig. 4, are taken. The horizontal distances are twice the actual distances on the glass plate.

Table I.

Run	t	n	Length of run	Bi	Bi_2
1	851°C	120.7 r.p.s.	12 hours	0.40	0.60
2	851	241.4	22	.40	.60
3	851	60.35	7	.40	.60
4	795	120.7	8	.30	.70

In all cases the experimental results would not agree with the theoretical distribution for Bi or Bi_2 as given by Eq. (8). The work of Leu[9] on the magnetic deflection of bismuth suggests that the beam is composed of Bi and Bi_2. On the basis of this suggestion various percentages of Bi and Bi_2 were assumed and using Eq. (8) the resultant intensity distributions plotted. These distributions were then compared with the experimental results. The theoretical distribution which best fitted the experimental results is taken as the composition of the vapor stream.

In Fig. 4 the solid lines represent the theoretical distributions for the conditions of operation given in Table I. The circles represent the experimental results obtained from Run 1, and the crosses those from Run 2. The experimental points are in close agreement (within the experimental error) with the theoretically derived curve except for a few points on the high velocity side. These points disagree by an amount greater than the experimental error. The disagreement is probably due to the lack of a sharply defined molecular beam during the entire course of the experiment. It may also be due to a "slipping"

[9] Alfred Leu, Zeits. f. Physik **49**, 498 (1928).

Fig. 4 also gives the velocities corresponding to various displacements for a speed of rotation of 241.4 r.p.s.

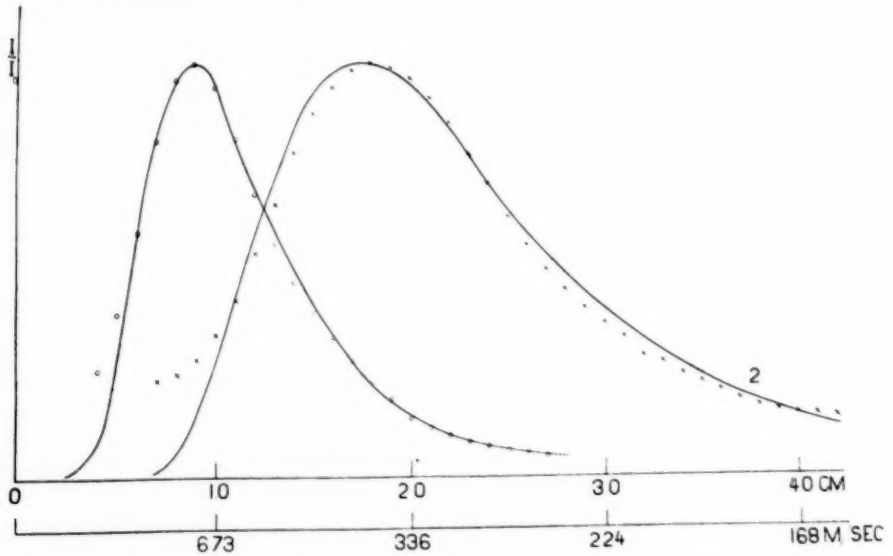

Fig. 4. Theoretical and experimental intensity distributions assuming a vapor composition of 40 percent Bi and 60 percent Bi_2. T equals 851°C. Curve 1, $n=120.7$ r.p.s., curve 2, $n=241.4$ r.p.s. Bottom line gives the molecular velocity corresponding to several displacements at a cylinder speed of 241.4 r.p.s.

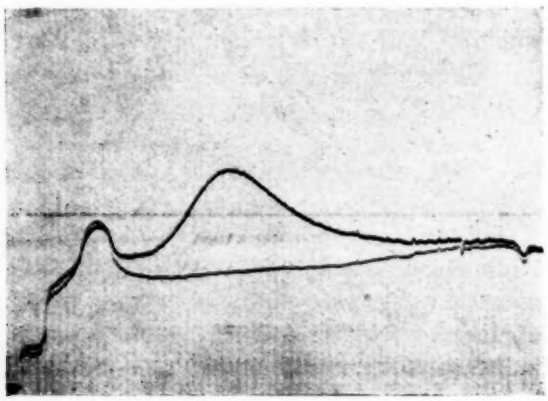

Fig. 5. Contact print of photometer record of Run 1, $n=120.7$ r.p.s. Abscissas twice actual deflections.

TABLE II

Displacement interval	Velocity band
1.0–1.1 cm	61 m/sec
2.0–2.1	15
3.0–3.1	7
4.0–4.1	4

of the molecules forming the zero mark. This possibility is being investigated.

Table II gives several displacement intervals of 1 mm width and the velocity band covering that interval. The high resolution is quite evident.

As Leu[9] observed, the dissociation of Bi_2 increased with the temperature and at about the same rate. His results disagree among themselves at the same temperature by 10 percent in some cases. If there is no "slipping" of molecules on the plate a variation in the composition of the vapor of less than 5 percent is detectable in this experiment and this method thus forms a more accurate means for the study of the dissociation of certain vapors, the results of which can be applied to calculating the heat of dissociation.

Errors

The temperature and speed could be kept constant to within one percent although it is doubtful if the temperature itself could be read accurately to within several percent. A possible source of error is that not all the molecules striking the plate remain there. It is possible that some escape, however this number is assumed to be negligible. It is not so certain that all molecules striking the plate remain at the point where they first make contact. There is the possibility for surface motion or "slipping." Evidence for a small amount of surface motion on fixed plates is presented by Cockcroft.[10] Any motion of the molecules on the glass plate due to the high speed of rotation must be negligible since the results obtained from Runs 1, 2, and 3, taken at the same temperature but at different speeds, indicate the same percentage vapor composition.

A test showed that no error is introduced in assuming that the electrometer deflections on the photometer records are directly proportional to the densities of the deposits.

Conclusion

A method is described for the direct measurement of molecular velocities. Results are presented in which the molecules are spread over a distance of more than 4 cm at a cylinder speed of 241.4 r.p.s. with an error of less than 5 percent. This resolution is many times that obtained by Stern, an analysis of the distribution of the deposit being impossible from his results, and several times that obtained by Eldridge who spread a velocity band of 900 to 200 meters per second over a plate length of 1 cm while in this experiment a velocity band of 673 to 168 meters per second is spread over 3 cm.

It is a pleasure to acknowledge my gratitude to Professor Elmer E. Hall under whose direction the problem was undertaken, for his advice and inspiration; to Professor Leonard B. Loeb for the many helpful discussions and encouraging remarks, and to Mr. G. P. Kraus, mechanician, for his willing cooperation in the mechanical details.

[10] J. D. Cockcroft, Proc. Roy. Soc. **A119,** 293 (1928).

THE AMPLIFICATION OF SMALL DIRECT CURRENTS

By Lee A. DuBridge
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Abstract

A new type of thermionic tube recently described by Metcalf and Thompson has made it possible for the first time to construct d.c. amplifying circuits with a current sensitivity exceeding that of any form of electrometer except the Hoffman; and with a ruggedness and dependability unattainable with any form of sensitive electrometer. The circuits are easily constructed and simple to operate. Three types of circuits have been tested out and are described. (1) A simple single-tube circuit with a Type R galvanometer has been found satisfactory for measurements of currents as small as 10^{-14} amp. (2) A two-tube bridge circuit gives greater stability and will easily measure currents of 10^{-16} amp. It has been found capable of detecting currents of 5×10^{-18} amp. (3) A two-stage circuit, using one of the new tubes and one of the UX-112A type, will amplify currents of 10^{-14} amp to such a value that they may be read on a microammeter.

Introduction

THERE is considerable interest among physicists in the possibility of using thermionic tubes for the amplification of very small direct currents, such as photo-currents, ionization currents, and currents due to electron or positive ion beams of various sorts. A number of different circuits have been described in the literature[1] by means of which ordinary radio tubes or screen grid tubes may be employed for this purpose; and while a number of observers have had considerable success in their use, for the most part the electrometer is still the instrument universally employed for measurements of this type.

The difficulties encountered in d.c. amplification are due largely to the fact that practically all thermionic tubes now available have been designed for amplification of rapidly varying currents, and possess characteristics which make them unsuitable for d.c. work. Only a few attempts have been made to design a tube particularly adapted to amplifying direct currents smaller than about 10^{-11} amp. However, very recently Metcalf and Thompson of the General Electric Laboratories have described[2] a new form of tube (the "FP-54 pliotron") particularly designed for this purpose and which is capable of amplifying currents as small as 10^{-17} amp. With this type of tube it is possible for the first time to construct an amplifying circuit with a sensitivity equaling or exceeding that of the best Compton electrometers, and at the same time possessing a ruggedness and dependability unattainable with these instruments. The present paper is an account of some further experi-

[1] See especially, Bennett, Rev. Sci. Inst. **1**, 466 (1930); Dearle and Matheson, Rev. Sci. Inst. **1**, 215 (1930); Razek and Mulder, J.O.S.A. and R.S.I. **18**, 460 (1929); Nelson, Rev. Sci. Inst. **1**, 281 (1930); also refs. 4 and 5 below.

[2] Metcalf and Thompson, Phys. Rev. **36**, 1489 (1930).

ments which have been made with these tubes to investigate their possibilities and limitations under actual working conditions, and to study the circuits in which they can be most efficiently used. An attempt has been made to present the results in a rather detailed and elementary way, so that physicists unfamiliar with vacuum tube technique may be aided in building workable amplifier circuits. The experiments were carried out at the General Electric Research Laboratories during the past summer, at the suggestion and under the direction of Dr. A. W. Hull, to whom the author is very greatly indebted.

It may be well to recall some of the requirements which must be met by circuits to be used for d.c. amplification.[3] Suppose, for example, that it is desired to amplify a current from, say, a photoelectric cell, using a standard

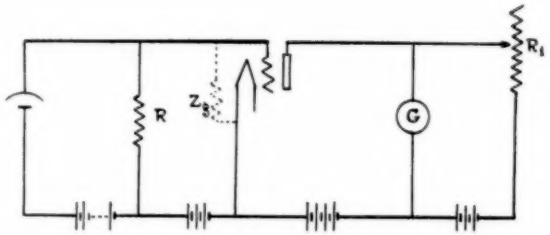

Fig. 1. Simple circuit for d.c. amplification.

circuit such as is represented in Fig. 1. With the photo-cell dark let the resistance R_1 be adjusted so that the galvanometer reads zero. If the photo-cell is then illuminated, the photoelectric current will cause a drop in potential across the grid resistance R, and this will be impressed on the grid of the vacuum tube. The resulting change in plate current will cause a deflection d of the galvanometer, given by

$$d/\sigma = i_G = \Delta i_p = g_m \Delta e_g$$

where σ is the sensitivity of the galvanometer (in mm/amp), $g_m = di_p/de_g$, the mutual conductance of the tube, and Δi_p and Δe_g the changes in plate current and grid potential, respectively. (It is assumed in setting $i_G = \Delta i_p$ that the resistance R_1 is considerably larger than the galvanometer resistance,[3] a condition always satisfied in practice). The voltage sensitivity S_v of the circuit, in mm/volt, then will be,

$$S_v = d/\Delta e_g = g_m \sigma. \tag{1}$$

To attain a high sensitivity to *voltage*, one would choose a tube of high mutual conductance and use it with a sensitive galvanometer. For our present purpose, however, we are more interested in the sensitivity to *current*, since the voltage applied to the grid may be made as large as we please, within limits, by simply increasing R. Since then, $\Delta e_g = Ri$, we have for the current sensitivity, S_i, (in mm/amp),

$$S_i = d/i = g_m R \sigma = S_v R. \tag{2}$$

[3] For a more detailed discussion see Nottingham, Jour. Frank Inst. **209**, 287 (1930).

Therefore, to attain a high *current* sensitivity it is necessary to use also a high value of R. This is the point at which circuits using ordinary radio tubes are severely limited. For it will be seen that the external resistance R is shunted by the grid resistance Z_g of the tube itself, and hence the total resistance cannot be made larger than Z_g. Now in ordinary tubes Z_g is not greater than a few hundred megohms, due to insulation leakage in the tube, to the collection of positive ions by the grid, and other causes. The first requirement, therefore, of a tube used to amplify very small currents is that the input resistance be very high, or what amounts to the same thing, that the grid currents in the tube under normal operating conditions be very small. In the new tube developed by Metcalf and Thompson all sources of grid current have been systematically eliminated or greatly reduced, so that the residual currents are of the order of 10^{-15} amp and the input resistance of the order of 10^{16} ohms. These tubes are therefore capable of giving enormously greater current sensitivity than has heretofore been possible.

In addition, since the tubes operate at a plate potential of only 6 volts, it is feasible to use large capacity storage batteries for a voltage supply, thus greatly reducing galvanometer fluctuations due to changes in battery voltages. The increased steadiness makes it possible to use a more sensitive galvanometer and thus makes up for the fact that the mutual conductance is somewhat lower than in ordinary tubes.

The FP-54 pliotrons are four-element tubes with two grids interposed between filament and plate. The inner grid serves as a space charge grid and the outer grid as a control grid. The normal operating conditions are:

Filament voltage	2.5 volts
Filament current	0.11 amps
Space charge grid	+4.0 volts
Control grid	−4.0 volts
Plate	+6.0 volts

Under these conditions the tubes have the following average characteristics:

Grid input resistance	10^{16} ohms (approx.)
Control grid current	10^{-15} amp (approx.)
Mutual conductance	25 microamp/volt
Plate current	40 microamp
Plate resistance	40,000 ohms
Voltage amplification factor	1
Grid capacity	3 $\mu\mu$F.

Circuits for Use with FP-54 Pliotrons

It is not necessary to develop new types of circuits for use with the new tubes, for it has been found that standard circuits are quite adequate. For a given current sensitivity, of course, a much simpler type of circuit can be used than would be necessary with ordinary tubes. An excellent summary of the theory and practice of d.c. amplification, using ordinary tubes, has been given by Nottingham,[3] and all of the circuits used in this investigation have been

described in detail in his paper. Slight modifications are necessary, due to the fact that the FP-54 is a four-element tube.

1. *The single-tube circuit.* A very simple type of circuit which has been found suitable for many ordinary current measurements is shown in Fig. 2. It is a standard type of single-stage d.c. amplifier, in which the plate current

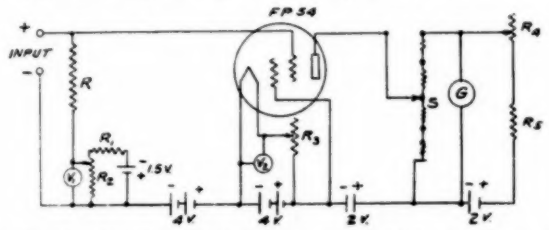

Fig. 2. Single tube circuit using FP-54 Pliotron. R, high resistance, 10^7-10^{11} ohms: R_1, fixed resistance, 100 ohms: R_2, 400 ohm potentiometer: R_3, 20 ohm rheostat: R_4, 10,000 ohm rheostat: R_5, fixed resistance, 40,000 ohms: V_1, 0–200 millivoltmeter: V_2, 0–5 voltmeter; S, Ayrton shunt.

is balanced out of the galvanometer by means of an auxiliary battery and rheostat. The numerical values of the various resistances used are given in the figure for convenience, though these are not at all critical, and will vary for different tubes.

The method of operation is as follows: With the tube operating at normal voltages the galvanometer is made to read zero by adjustment of the rheostat R_4. The voltage sensitivity of the circuit is then determined by applying to the control grid a series of known voltages by means of the potential divider, R_2, and observing the corresponding galvanometer deflections. If the deflection is then measured for an unknown input current i, the magnitude of i can at once be determined if R is known. There is a linear relation between galvanometer deflection and input voltage as long as the latter does not exceed about 300 millivolts, in spite of the fact that the tubes do not operate normally on the straight part of their characteristic.

The circuit may be made independent of the tube characteristics by using a null method, in which the galvanometer deflection due to the input current is brought back to zero by applying a compensating voltage e by means of R_2. The input current is then simply equal to e/R. The *accuracy* then attainable is limited only by the accuracy of the voltmeter V_1, the accuracy with which R is known, and the precision with which the galvanometer can be set to zero.

The highest voltage sensitivity which can be attained with such a circuit is limited by the fluctuations due to changes in battery voltages and other causes. By using large storage batteries (e.g. 90 amp–hr) for the voltage supply and by careful shielding it has been found possible, with a Leeds and Northrup Type R galvanometer, ($1/\sigma = 5\times10^{-10}$ amp/mm), to obtain a stable voltage sensitivity in excess of 50,000 mm/volt. With a resistance R of 10^{13} ohms, a current sensitivity ($=1/S_i$) of 2×10^{-15} amp/mm is attained. Accurate measurements (to better than 1 percent) can then be made of currents of 10^{-13} amp or larger. This is just about the order of magnitude of the currents usually measured in electrometer circuits.

A somewhat higher current sensitivity may be obtained by "floating" the control grid, i.e., by making R infinite. The residual grid currents within the tube will then cause the grid to charge up slowly, and a steady drift of the galvanometer is observed. The rate of change of grid voltage will be i_g/C, where i_g is the grid current and C is the electrostatic capacity of the grid circuit. For the FP-54 tubes the grid current is in the neighborhood of 10^{-15} amp and the capacity of the grid itself is about $3\mu\mu$F. If the remainder of the grid circuit be assumed to have a capacity of 10 $\mu\mu$F, and if the voltage sensitivity, S_v, is 10^5 mm/volt, then the rate of drift of the galvanometer will be approximately 7.7 mm/sec. This drift is normally very constant, so that an input current as small as 10^{-16} amp can be measured by noting the *change* in the rate of drift which it causes. This is the method used in the General Electric Laboratories for measuring the grid currents in the tubes as they come from the factory.

2. *Balanced tube circuit.* It was found that, when currents of 10^{-14} amp or less are to be measured, more satisfactory operation is obtained with a two-tube circuit of the type developed by Wold, Wynn-Williams[4] and Eglin.[5] This method is also more satisfactory for measurement of larger currents where great steadiness and precision are desired. A diagram of the circuit actually used is shown in Fig. 3. It will be noted that it is essentially a Wheat-

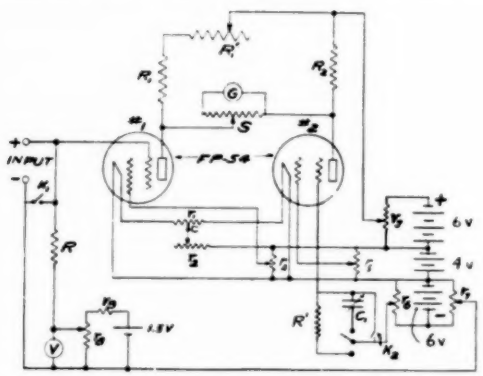

Fig. 3. Two-tube bridge circuit. R, R', high resistances: R_1, fixed resistance, 5000 ohms: R_2, fixed resistance, 10,000 ohms: R_1', resistance box, 10,000 ohms: r_1, 2 ohm rheostat: r_2, 20 ohm rheostat: r_3 to r_8, 400 ohm potentiometers: r_9, fixed resistance, 1000 ohms: K_1, K_2, electrometer keys: V, millivoltmeter: S, Ayrton shunt: C_1, variable air condenser, 15$\mu\mu$F.

stone bridge, with amplifier tubes in two of the arms and resistances in the other two. When this circuit is properly balanced it can be shown[3] that the galvanometer will be unaffected by fluctuations in the battery voltages. A considerably greater steadiness is thereby attained, so that a galvanometer of higher sensitivity may be used and a higher stable voltage sensitivity obtained. It was found, in fact, that satisfactory operation could be maintained

[4] Wold, U. S. Patent 1232879 (1916). Wynn-Williams, Proc. Camb. Phil. Soc. **23,** 810 (1927); Phil. Mag. **6,** 324 (1928).

[5] Eglin, Jour. Opt. Soc. **18,** 393 (1929).

at a sensitivity of 250,000 mm/volt, using a galvanometer sensitivity of $1/\sigma = 5\times10^{-11}$ amp/mm.

The method of balancing is as follows:[3] With the tubes operating at normal voltages, R_1' is adjusted to bring the galvanometer to zero. By means of r_3 a small change is then made in the plate voltage and the effect on the galvanometer noted. R_1' is then changed by, say, 1000 ohms and the galvanometer brought back to zero by adjustment of the various grid potentials. The plate potential is again changed by the same amount as before, and if the resulting galvanometer deflection is smaller, R_1' has been altered in the right direction. The process is then repeated until a change in plate potential produces no effect on the galvanometer.

In a similar manner the effect of filament voltage changes is observed by varying r_2, and a position of the contact C on r_1 is found such that small variations in r_2 produce no effect on the galvanometer. During this adjustment R_1' is left fixed and the balance restored after each change of C by manipulation of the grid potentials. The circuit is now ready for operation, and may be calibrated in the same way as the single-tube circuit.

The circuit shown in Fig. 3 was designed so that it could be used either with the steady deflection method or the rate of drift method. If only the steady deflection method is to be used the condenser C_1 may be eliminated and if only the rate of drift method is to be used, the resistances R and R' may be eliminated. In either case the operation is similar to that of the single-tube circuit, tube No. 1 being the active tube and No. 2 acting merely as a "dummy." The resistance R' in the grid circuit of the second tube makes for greater symmetry and hence increases the stability somewhat, but in many cases it may be left out and the grid connected directly to r_6. If R is 10^{10} ohms and the voltage sensitivity 250,000 mm/volt, the current sensitivity, $1/\sigma$, will be 4×10^{-16} amp/mm. Still higher resistances may of course be used.

An exceedingly high sensitivity may be obtained with this circuit using the rate of drift method of measurement. If the grids of both tubes are floated, and if they both charge at the same rate, then there will be no effect on the galvanometer. In general, however, the grid currents of two tubes will not be the same, but the rate of charge of the two may be *made* the same by increasing the capacity of one grid. This was accomplished by introducing the variable 15$\mu\mu$F condenser[6] C_1 in the grid circuit of the second tube. The tube with the largest grid current was made No. 2 in the circuit. This condenser was then adjusted until the galvanometer showed no drift. If a current i is now started in the input circuit, this will change the rate of charge of the grid of the first tube and hence give a galvanometer drift which is proportional to i.

The smallest current which can be detected by this method is limited only by the fluctuations of the circuit. The effects of external electric and magnetic fields, especially rapidly varying fields, were carefully eliminated by enclosing the entire circuit in a metal container which was almost air tight. All

[6] A satisfactory condenser was made by taking an ordinary radio condenser and replacing the bakelite insulation by quartz.

rheostats and connections should of course make positive contact; the storage batteries must be in good condition; to prevent insulation leaks the tubes must be kept dry. It was even found necessary to eliminate effects due to residual ionization of the air by enclosing the control grid leads in small quartz tubes painted on the outside with a suspension of graphite ("aquadag"). A wide band of aquadag was also painted around the tubes themselves to serve as a guard ring. When all these precautions were taken, it was found that the residual fluctuations were sufficiently small that an input current of approximately 5×10^{-18} amp could be detected and measured. Such a current produced a galvanometer drift in the circuit used of about 10 mm/min, and the fluctuations were also of this order. These fluctuations were of the order of magnitude to be expected from shot-effect fluctuations in the control grid currents in the two tubes, and hence the limit of sensitivity of the tubes was approximately attained.

It is of interest to note that a current of 5×10^{-18} amp is only 30 electrons per second, and the shot-effect fluctuations in such a current over a period of one second are of the order of 15 percent. If tubes could be constructed in which the grid currents were as low as 10^{-17} amp (and this may not be impossible) the sensitivity limit of the amplifier could be pushed to 5×10^{-19} amp, or 3 electrons per second. If a short period galvanometer were used, individual electron pulses could be observed.

It will be noted that the maximum voltage sensitivity attainable with this circuit is about five times that attainable with the Compton electrometer, and is 25 to 50 times greater than the usual operating sensitivity of the electrometer. There is an even greater difference between the current sensitivities of the two instruments, due to the smaller capacity of the amplifier. The author has found that, roughly speaking, a well-built amplifier is as stable at a sensitivity of 100,000 mm/volt as a good Compton electrometer at 5,000 mm/volt. In addition the amplifier has the advantages of greater mechanical ruggedness and short period. Furthermore, the sensitivity of the amplifier circuit has been found to remain constant over long periods of time, in contrast to the frequent adjustments of quadrant and needle required to maintain a constant high sensitivity of an electrometer. In short the amplifying circuit herein described has been found to be a practical and convenient current-measuring device,[7] with an attainable sensitivity greater than that of any known instrument, with the exception of the Hoffman electrometer and the Geiger counter.

3. *The two-stage amplifier.* For many problems it is desirable to measure very small currents, such as photoelectric currents, but at the same time to use an extremely rugged meter.[8] In order to test out the possibility of using instruments still more rugged than the Type R galvanometer, a two-stage

[7] Such a circuit is now being used successfully by Professor G. E. M. Jauncey and Mr. W. D. Claus at Washington University for measurements of ionization currents in an x-ray spectrometer.

[8] This is true, for example, in the photoelectric photometry of stars, where the measuring Instrument must be mounted directly on the telescope.

amplifier circuit shown in Fig. 4 was constructed. By employing a UX-112A tube in the second stage it is possible to measure the output with an ordinary microammeter (0–100 μ amp). A second state of amplification could of course be employed with either of the two circuits previously described. It seemed, however, that the greatest simplicity and convenience could be attained by using in the first stage a balanced circuit in which the dummy tube is replaced by a variable resistance. In place of the galvanometer, the second stage of amplification is substituted.

It is evident that the requirements for the tube to be used in the second stage are quite different from those for the first stage. For, while the chief requirement for the first stage is a high grid resistance, this is not at all necessary in the second stage, since the resistances R_1 and R_2 are relatively small. One will therefore use in the second stage a tube of high mutual conductance.

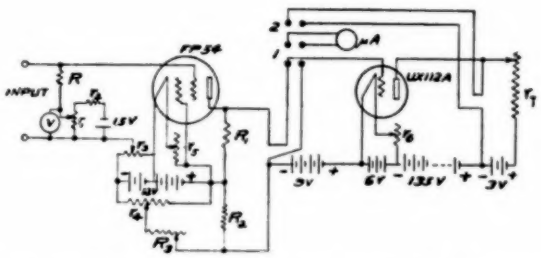

Fig. 4. Two-stage amplifier. R_1, R_2, Fixed resistances, 10,000 ohms: R_3, variable resistance, 20,000 ohms: r_1, r_3, r_4, 400 ohm potentiometers: r_2, fixed resistance, 1000 ohms: r_5, 60 ohm rheostat: r_6, 6 ohm rheostat: r_7, rheostat with fine adjustment, 1000 ohms: R, high resistance, 10^7–10^{11} ohms.

If a voltage e is applied to the grid of the first tube, then the change in the voltage of the grid of the second tube will be ke, where k stands for the expression

$$\mu R_p/(R_p + r_p).$$

Here μ is the voltage amplification factor of the first tube, R_p the external resistance in the plate circuit, and r_p the internal impedance of the first tube. The change in the plate current of the second tube will then be

$$\Delta i_p = g_{m2} ke$$

where g_{m2} is the mutual conductance of the second tube. This change in plate current will be read on the microammeter. Now the voltage amplification obtained by the FP-54 in the circuit shown is actually less than 1, so that if another FP-54 were used in the second stage, the overall sensitivity of the combination would be less than for a single tube. However, if a tube of large mutual conductance is used in the second stage, an increase in sensitivity is obtained. With the circuit shown in Fig. 4 the over-all sensitivity was found to be approximately 375 microamp/volt. Using an input resistance, R, of 10^{11} ohms, an output current of 1 microamp was obtained for an input current of 2.7×10^{-14} amp. This is a current amplification of 3.75×10^7.

The method of operating the circuit is as follows: With the double-pole-double-throw switch in position 1, the microammeter reads the output of the first stage only. The first stage is then balanced until the meter reads zero. The balance is obtained in a manner similar to the balance of the two-tube circuit by adjustment of R_3 and r_4. The microammeter switch is then thrown to position 2 and r_5 adjusted until the meter again reads zero. The circuit is then ready for operation.

The usefulness of such a circuit is quite apparent for problems in which ruggedness, portability or economy are of importance. A very inexpensive microammeter may be used since it serves only as an indicating instrument, and will be calibrated in terms of input voltage by means of the potentiometer r_1 and voltmeter V.

As a test of the practical use of this circuit the input terminals were connected to a G.E. caesium photoelectric cell, type UX-867, illuminated by a small headlight lamp. An output current of several microamperes was observed when the lamp filament was at a temperature such that it was scarcely visible to the eye in a dimly lighted room.

There are many variations and improvements on the two-stage circuit which at once suggest themselves. The circuit shown in Fig. 4 was chosen primarily for its simplicity, and it is described here because it was found to give quite satisfactory operation. Its stability and sensitivity could undoubtedly be improved by using a complete two-tube bridge circuit in each stage, using two FP-54 tubes in the first and two UX-112A tubes in the second stage.

4. *General precautions.* The chief purpose of the present paper is to bring out the fact that with the new FP-54 pliotrons the construction of a highly sensitive d.c. amplifier has been made a relatively simple task. It may be well to remark, however, that *regardless of the instrument used to measure or detect small currents*, the circuits which carry them must always be insulated and shielded with the greatest care. The problem of shielding is of even greater importance for an amplifier circuit than for an electrometer. This is due to the fact that an electrometer is practically insensitive to high frequency electric fields of constant intensity, while the amplifier actually serves as a detector for such fields. Air-tight shielding of the grid circuits is therefore essential if the amplifier is to be used in the vicinity of high voltage equipment (e.g., x-ray tubes). Shielding of *all parts* of the amplifier circuit is advised.

In all other respects (such as choice of insulation material, construction of grounding keys and high resistances, etc.) the grid circuits of an amplifier may be treated exactly as an electrometer circuit of equal sensitivity. It has been found necessary to operate the tubes at their rated voltages for from half an hour to two hours before readings are begun, in order that temperature equilibrium be obtained and that the electrostatic charges on the walls of the tubes and other places shall have reached a steady state.

A MACHINE FOR AUTOMATIC GENERATION OF AIRFOILS

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Abstract

The present paper is a short account of work done with the purpose of adapting the speed, accuracy, reproducibility, and system which a drawing machine is capable of delivering to drawing large sets of systematically varied airfoils for wind tunnel research. An airfoil is defined in the paper merely as a closed curve without discontinuities in curvature and with a sharp trailing edge. Use is being made of the fact that such curves are produced by kinematical mechanisms as trajectories or coupling curves for pencil points on or near the polar curve. A machine based on the four member linkage is described and a table showing a set of systematically varied airfoils obtained with the machine is reproduced.

PRESENT methods of mechanical and analytical generation of airfoils assume a function of a complex variable to be responsible for the particular airfoil. The airfoil appears as the closed streamline in the conformal representation of a flow around a circle or some other contour, the flow around which is already known. Thus the airfoils of Zoukowsky, Drzewiecki, Miller and others have been calculated analytically and scattered attempts were made to build machines capable of delivering the particular transformation of a circle or ellipse. This mechanical-analytical method of approach has the advantages of permitting calculation of flow around the airfoil and forces acting upon it on the basis of frictionless incompressible fluid theory.

There exists however the possibility of a different viewpoint on the problem: airfoils can be defined merely as closed curves without discontinuities in curvature having a "sharp" trailing edge, the latter being, according to Prandtl's theory of boundary layer, the essential requirement for maintenance of circulation in the viscous, actual fluid. Decision as to their efficiency is left with the experimental methods. A machine capable of drawing such curves can be regarded as a mathematical operator applied to a certain closed curve described by the primary point (point A on Fig. 1, say) of the machine; this mathematical (or rather physical) operator is defined by the parameters of the machine. The transformation function drops out of the picture, at least when not expressly required, and the determination of aerodynamical qualities of the airfoil is left with the experiment.

Justification of this method of approach is its simplicity, speed and accuracy as well as efficiency of the drawing machines regarding reproducibility and systematization.

Kinematical considerations concerning shape of coupling curves of mechanisms[1] lead to the conclusion that machines having two branches of their

[1] L. Burmester, Lehrbuch der Kinematik. Felix, Leipzig, p. 297 (1888).

polar trajectory in the domain of the drawing table will draw airfoil-shaped curves (in the sense defined), for points of the movable plane situated upon or near the so-called polar curve.[2] The theory of certain linkages has been brought to a high degree of perfection. Unfortunately the most practical and inspiring problem which worried early investigators was that of securing a trajectory with the best approximation to the straight line (for mechanical engineering problems).

In the following a machine based essentially upon the classical four-member linkage is described.

The particular four-member linkage, one of the four possible combinations, is drawn in Fig. 1. Here the arm OA rotates while the other arm, BC, performs oscillations around its hinge, without making a complete turn. The instantaneous center of rotation or pole P is found at the intersection of the

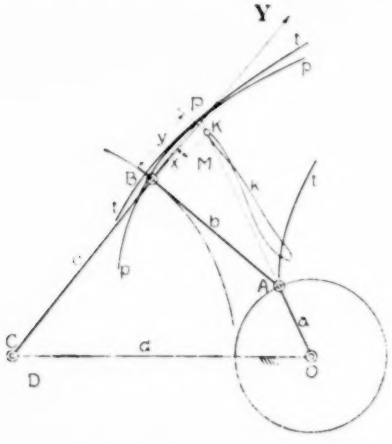

Fig. 1. The four-member linkage.

radii OA and CB. The polar trajectory,[2] t, is obtained by connecting the successive positions of the pole on plane D. It has been drawn in the figure and one observes that it crosses the drawing table twice. The polar curve, p, is also drawn. It is[3] a bicircular curve of the eighth order and is conveniently located with respect to the rod AB. Burmester[4] shows that the coupling curves of this mechanism are of the sixth order. This together with a wide variation possibility points to the suitability of the mechanism for plotting airfoils.

An experimental model of the airfoil plotting machine is shown in Fig. 2. For fixed values of dimensions, $a = OA$, $b = AB$, $c = BC$ and $d = CO$, coupling curves were drawn for various positions of the pencil K. These positions were

[2] Under polar trajectory is understood the locus of instantaneous centers of rotations, of the movable plane relative to the drawing table, upon the drawing table. The polar curve represents the locus of instantaneous centers of rotation upon the movable plane.

[3] R. Müller, Zeits. f. Math. u. Physik **36,** 11–20 (1891); **34,** 303–305 and 372–375 (1889); **42,** 247–271 (1897).

[4] Burmester, reference 1, 305.

characterized by the pencil point coordinates x and y with origin at B and X and Y axes along AB and BY respectively. The procedure of drawing consisted in slowly rotating the arm OA slightly over one full turn. Airfoils were plotted for position of the pencil not far from the polar curve on sheets of paper fixed to the drawing table.

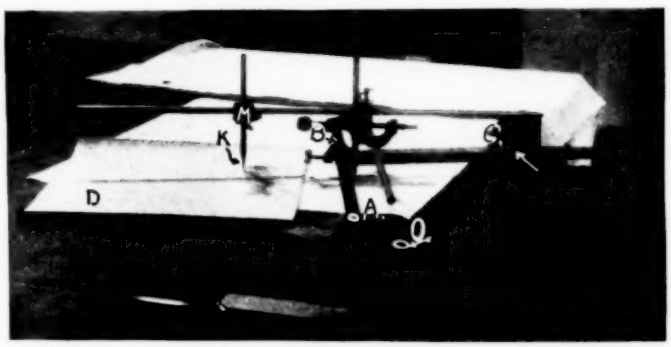

Fig. 2. The experimental model of the airfoil drawing machine.

Each airfoil is thus characterized by six parameters showing the dimensions of a, b, c, d, x and y. Any airfoil can be easily reproduced by merely setting the machine to the desired values of the parameters.

Results

A set of airfoils is shown on Fig. 3. It has the following values of the parameters: $a=3$, $b=14$, $c=9$, $d=18$, x and y variable. The curves were filled in with india ink and arranged in a two dimensional scheme according to the

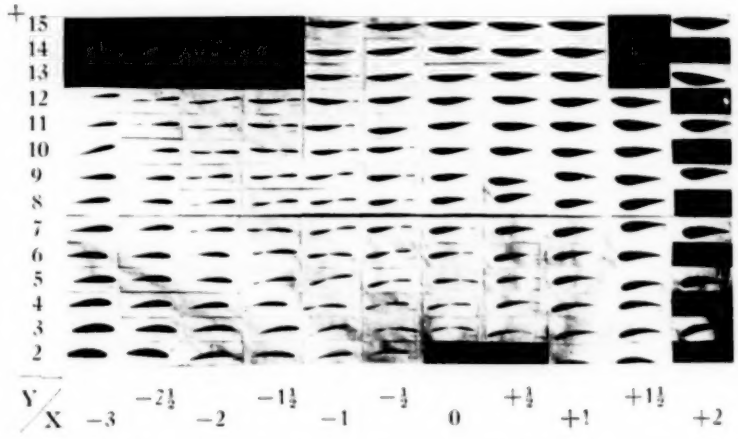

Fig. 3. A family of airfoils drawn by the machine. The photograph is considerably reduced.

variable parameters x and y. Each of the twins appearing in the center region of the set should be regarded as an airfoil with finite trailing edge angle. The analytical nature of curves drawn by the machine permits but zero angle trailing edge for single curves.

Several more promising airfoils are reproduced on Figs. 4 and 5.

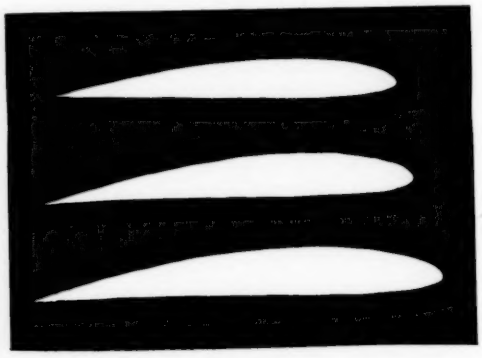

Fig. 4. Three full-scale drawings of airfoils plotted by the machine ($x=-1\frac{3}{4}$; $y=7, 6, 5$, the largest airfoil corresponding to the smallest y).

Fig. 5. Airfoil $x=2\frac{1}{2}$, $y=7$.

As a rule the accuracy of plotting was well within $\frac{1}{4}$ percent of the chord.

A machine of the type described permits drawing of a set of 150 airfoils in the course of a few days. With balance plotting automatically the polar diagram and with automatic model making machinery (as designed by the writer) the total time and expenditure connected with the investigation of properties of a large set of airfoils can be reduced to a very reasonable figure.

RECIPROCAL RELATIONS IN IRREVERSIBLE PROCESSES. I.

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Abstract

Examples of coupled irreversible processes like the thermoelectric phenomena, the transference phenomena in electrolytes and heat conduction in an anisotropic medium are considered. For certain cases of such interaction reciprocal relations have been deduced by earlier writers, e.g., Thomson's theory of thermoelectric phenomena and Helmholtz' theory for the e.m.f. of electrolytic cells with liquid junction. These earlier derivations may be classed as quasi-thermodynamic; in fact, Thomson himself pointed out that his argument was incomplete, and that his relation ought to be established on an experimental basis. A general class of such relations will be derived by a new theoretical treatment from the principle of microscopic reversibility. (§§1–2.) The analogy with a chemical monomolecular triangle reaction is discussed; in this case a a simple kinetic consideration assuming microscopic reversibility yields a reciprocal relation that is not necessary for fulfilling the requirements of thermodynamics (§3). Reciprocal relations for heat conduction in an anisotropic medium are derived from the assumption of microscopic reversibility, applied to fluctuations. (§4.) The reciprocal relations can be expressed in terms of a potential, the dissipation-function. Lord Rayleigh's "principle of the least dissipation of energy" is generalized to include the case of anisotropic heat conduction. A further generalization is announced. (§5.) The conditions for stationary flow are formulated; the connection with earlier quasi-thermodynamic theories is discussed. (§6.) The principle of dynamical reversibility does not apply when (external) magnetic fields or Coriolis forces are present, and the reciprocal relations break down. (§7.)

I. Introduction

WHEN two or more irreversible transport processes (heat conduction, electrical conduction and diffusion) take place simultaneously in a thermodynamic system the processes may interfere with each other. Thus an electric current in a circuit that consists of different metallic conductors will in general cause evolution or absorption of heat at the junctions (Peltier effect). Conversely, if the junctions are maintained at different temperatures an electromotive force will usually appear in the circuit, the thermoelectric force: the flow of heat has a tendency to carry the electricity along.

In such cases one may naturally suspect reciprocal relations by analogy to the reciprocal relations which connect forces and displacements in the equilibrium theory of mechanics and in thermodynamics. Relations of this type have been proposed and discussed by many writers. The earliest of them all is due to W. Thomson;[1] it deals with thermoelectric phenomena. We shall cite Thomson's reciprocal relation in a simple form as a symmetry condition for the relations which connect the forces with the velocities. The electric current we shall call J_1, the heat flow J_2. The current is driven by the elec-

[1] W. Thomson (Lord Kelvin), Proc. Roy. Soc. Edinburgh 1854, p. 123; Collected Papers I, pp. 237–41.

tromotive force, which we shall call X_1. In corresponding units the "force" which drives the flow of heat will be:

$$X_2 = -\frac{1}{T}\,\text{grad}\ T,$$

where T denotes the absolute temperature (Carnot). If the heat flow and the current were completely independent we should have relations of the type:

$$X_1 = R_1 J_1$$
$$X_2 = R_2 J_2$$

where R_1 is the electrical resistance and R_2 a "heat resistance." However, since the two processes interfere with each other we must use the more complicated phenomenological relations

$$\begin{aligned} X_1 &= R_{11} J_1 + R_{12} J_2 \\ X_2 &= R_{21} J_1 + R_{22} J_2. \end{aligned} \tag{1.1}$$

Here Thomson's contention is:

$$R_{12} = R_{21}. \tag{1.2}$$

Thomson arrived at this relation from thermodynamic reasoning, but he had to make one additional assumption, namely: "*The electromotive forces produced by inequalities of temperature in a circuit of different metals, and the thermal effects of electric current circulating in it, are subject to the laws which would follow from the general principles of the thermodynamic theory of heat if there were no conduction of heat from one part of the circuit to another.*" Thomson thought this assumption very plausible. Even so, he cautiously considered his reciprocal relation (1.2) a conjecture, to be confirmed or refuted by experiment, since it could not be derived entirely from fundamental principles known at that time. At present Thomson's relation is generally accepted, because it has been confirmed within the limits of error of the best measurements. As regards the theory, the same relation has frequently been found as a by-product of investigations in the electron theory of metals. However, Thomson's relation has not been derived entirely from recognized fundamental principles, nor is it known exactly which general laws of molecular mechanics might be responsible for the success of Thomson's peculiar hypothesis.

In the following, a general class of reciprocal relations in irreversible processes will be derived from the *assumption of microscopic reversibility*. No further assumptions will be necessary, except certain theorems borrowed from the general theory of fluctuations. Among the relations to be derived, many have been proposed before, but some will be new. An important group among these relations can be summarized in a variation-principle, which is nothing but an extension of Lord Rayleigh's "*principle of the least dissipation of energy*"; we shall retain the name for the extended principle. According to this theorem the *rate of increase of the entropy* plays the rôle of a potential.

Thomson's hypothesis covers only part of the cases which we are going to consider, yielding the same results as the more general "principle of the least dissipation of energy." This connection will be discussed in §6; here, however, we shall comment on the natural interpretation of Thomson's hypothesis, because his formulation is somewhat ambiguous: He assumes that the temperature differences present are bound to cause a certain degradation of energy by conduction of heat; if another irreversible process (electrical conduction) takes place simultaneously, this process must cause an additional degradation of energy, making the total rate of increase of the entropy greater than it would be by heat conduction alone.

The derivation of such results from the principle of microscopic reversibility will hardly be a surprise to workers who are acquainted with the theory of irreversible processes. In many familiar cases this principle guarantees an independent balancing of different classes of molecular processes maintaining a statistical equilibrium. The writer actually conceived the idea for the new derivation of reciprocal relations by comparing the relations due to Thomson,[1] Helmholtz[2] and others with the conditions for reversibility in certain chemical reactions, as presented in §3.

The principle of microscopic reversibility is less general than the fundamental laws of thermodynamics; the consequent limitations to our reciprocal relations will be briefly described in §7. It is easy to show that Thomson's relation is no thermodynamic necessity. According to (1.2) the rate of production of entropy per unit volume of the conductor equals

$$\frac{dS}{dt} = \frac{1}{T}(X_1J_1 + X_2J_2) = \frac{1}{T}(R_{11}J_1^2 + (R_{12} + R_{21})J_1J_2 + R_{22}J_2^2).$$

Thermodynamics requires only:

$$dS/dT > 0$$

identically, except when J_1 and J_2 vanish simultaneously, or, by simple algebra:

$$R_{12} + R_{21} < 2(R_{11}R_{22})^{1/2}. \tag{1.3}$$

This condition (in a somewhat different form) was given by Boltzmann.[3]

In the present communication only one special case, namely heat conduction in an anisotropic medium (crystal), will be adequately treated (§4). This limitation allows a simplified derivation, which nevertheless brings out clearly the essential ideas of the new theoretical treatment. The derivation of other reciprocal relations, including Thomson's, will be reserved for later publication; here we shall merely enumerate the most important cases.

2. Examples of Mutual Interaction of Irreversible Processes

The formulation (1.1) of the laws of irreversible processes in terms of resistances R_{11}, etc., is well adapted to a comparison with the thermodynamic requirements; but as a rule it is a little easier to see the physical meaning of such

[1] H. v. Helmholtz, Wied. Ann. **3**, 201 (1876); Wiss. Abh. **1**, 840.

[2] L. Boltzmann, Wien. Ber. **96**, 1258 (1887).

laws when they are expressed in terms of conductances L_{11}, L_{12} $\cdots$ etc.:

$$\begin{aligned} J_1 &= L_{11}X_1 + L_{12}X_2 \\ J_2 &= L_{21}X_1 + L_{22}X_2 \end{aligned} \tag{2.1}$$

where:

$$L_{11} = R_{22}/(R_{11}R_{22} - R_{12}R_{21})$$

etc. The reciprocal relation (1.2) takes the form:

$$L_{12} = L_{21}. \tag{2.2}$$

So far we have only mentioned the interaction of heat conduction and electrical conduction. In mixtures of gases and in solutions a third transport process is possible, namely diffusion. Experience shows that any two possible transport processes are likely to interfere with each other to some extent.

It is well known that an electric current in a conductor of the second kind causes transport of matter. Conversely, a concentration gradient between two identical reversible electrodes causes an electromotive force. The relations between "forces" and velocities may again be expressed in the form (2.1). J_1 may again be the electric current, and X_1 the e.m.f.; for J_2 we take the flow of solute relative to the solvent, for X_2 the gradient $-\operatorname{grad}\mu = X_2$ of the thermodynamic potential μ of the solute. The coefficients L_{11} $\cdots$ L_{22} are connected, in a manner which we need not discuss in detail, with the electrical resistance, the diffusion coefficient, the "transference number" and the e.m.f. caused by a given concentration gradient. Usually the fourth is not mentioned, since Helmholtz[3] has derived the reciprocal relation.

$$L_{12} = L_{21}. \tag{2.2}$$

His derivation is quite analogous to Thomson's treatment of the thermoelectric phenomena, and it suffers from the same weakness. However, the experiments confirm the result, Nernst[4] has given a kinetic derivation from assumptions that are somewhat specialized, and the theorem is generally accepted.

For the interaction between heat conduction and diffusion a reciprocal theorem has been derived by Eastman;[5] the case is quite analogous to the preceding. The diffusion caused by a temperature gradient is known as the Soret effect; the inverse effect has been demonstrated in a qualitative manner for a mixture of gases.[6] Eastman has also discussed thermoelectric forces in electrolytes. In that case three different transport processes are involved simultaneously. The phenomenological relations can be expressed in the form

$$\begin{aligned} J_1 &= L_{11}X_1 + L_{12}X_2 + L_{13}X_3 \\ J_2 &= L_{21}X_1 + L_{22}X_2 + L_{23}X_3 \\ J_3 &= L_{31}X_1 + L_{32}X_2 + L_{33}X_3 \end{aligned} \tag{2.3}$$

and we may suspect $3 \cdot 2/2 = 3$ reciprocal relations

$$L_{12} = L_{21}\ ;\ L_{13} = L_{31}\ ;\ L_{23} = L_{32}. \tag{2.4}$$

[4] W. Nernst, Zeits. f. physik. Chem. **2,** 613 (1888).

[5] E. D. Eastman, J. Am. Chem. Soc. **48,** 1482 (1926); **50,** 283, 292 (1928).

[6] Dufour, Arch. d. sc. phys. et nat. Genf **45,** 9 (1872); Pogg. Ann. **148,** 490 (1873).

The case of simultaneous diffusion of several substances in the same solution completes the list of possibilities for coupling between transport processes in isotropic bodies.

Transport processes in anisotropic bodies afford a few interesting examples of mutual interaction, for instance the conduction of heat in crystals of low symmetry. In the most general case of a triclinic crystal the phenomenological relations can be written in the form (2.3). We chose a cartesian frame of coordinates x_1, x_2, x_3; then J_1, J_2, J_3 are the components of the heat flow along these axes, and the "forces" are $X_1 = -(1/T)\partial T/dx_1$ etc. In a suitable frame of reference x_1^*, x_2^*, x_3^* parallel to the main axes of the ellipsoid:

$$L_{11}x_1^2 + (L_{12} + L_{21})x_1x_2 + \cdots + L_{33}x_3^2 = \lambda_1 x_1^{*2} + \lambda_2 x_2^{*2} + \lambda_3 x_3^{*2} = \text{const.} \quad (2.5)$$

the equations of heat conduction take the form

$$\begin{aligned} J_1^* &= \lambda_1 X_1^* + \omega_3 X_2^* - \omega_2 X_3^* \\ J_2^* &= -\omega_3 X_1^* + \lambda_2 X_2^* + \omega_1 X_3^* \\ J_3^* &= \omega_2 X_1^* - \omega_1 X_2^* + \lambda_3 X_3^*. \end{aligned} \quad (2.6)$$

If the reciprocal relations (2.4) are valid, then:

$$\omega_1 = \omega_2 = \omega_3 = 0 \quad (2.7)$$

and the conducting properties of the crystal are entirely determined by the ellipsoid (2.5); whenever the gradient of the temperature is parallel to one of the axes x^* the heat flows in exactly the same direction. If ω_1, ω_2, ω_3 do not vanish there may still be three such directions of direct heat flow, in which case these directions will no longer be perpendicular to each other, or there may be only one such direction. For instance, for crystals belonging to the tetragonal or hexagonal systems the inherent symmetry fixes the axes $x_1^* = x_1$; $x_2^* = x_2$; $x_3^* = x_3$ and demands certain relations between the coefficients, so that (2.3) and (2.6) take the form

$$\begin{aligned} J_1 &= \lambda_1 X_1 + \omega_3 X_2 \\ J_2 &= -\omega_3 X_1 + \lambda_1 X_2 \\ J_3 &= \lambda_3 X_3. \end{aligned} \quad (2.8)$$

If clockwise and counterclockwise rotations around the axis x_3 are equivalent ω_3 vanishes for reasons of symmetry, but certain classes of the crystallographic systems in question do not possess such a symmetry. When ω_3 does not vanish the flow of heat in the x_1, x_2 plane will always form an angle:

$$\arctan(-\omega_3/\lambda_1)$$

with the temperature gradient. If we should take a circular plate of such a crystal, cut parallel to the base (x_1, x_2 plane), and heat it in the middle, maintaining cylindrical symmetry, the heat would flow in spirals. Attempts by Soret and W. Voigt to detect this spiral motion met with negative results, in spite of a very sensitive method.[7]

[7] Ch. Soret, Arch. de Geneve **29,** no. 4 (1893); **32,** no. 12 (1894). W. Voigt, Gött. Nachr. 87, (1903).

The case of electrical conduction in highly anisotropic crystals is quite analogous to the heat conduction, and the thermoelectric phenomena in crystals afford a variety of possibilitities for reciprocal relations. We need only mention these two examples; a detailed discussion would not bring out any new features of the general problem.

3. Analogy with Chemical Reactions

We shall compare (2.3) with the equations for a chemical monomolecular triangle reaction. Suppose that a certain substance may exist in a homogeneous phase in three different forms A, B, C. Suppose further that any one of these may spontaneously transform itself directly into either of the others according to the scheme

$$\begin{array}{ccc} A & \searrow & \\ \uparrow\downarrow & & B \\ C & \nearrow & \end{array} \tag{3.1}$$

We shall assume that the reactions obey a simple mass-action law. That is, the fraction of A molecules which will change into B in a given short time Δt is

$$k_{BA}\Delta t$$

where k_{BA} is a constant. Then the rates of change of the amounts n_A, n_B, n_C are given by the equations

$$\begin{aligned} \frac{dn_A}{dt} &= -(k_{BA} + k_{CA})n_A + k_{AB}n_B + k_{AC}n_C \\ \frac{dn_B}{dt} &= k_{BA}n_A - (k_{AB} + k_{CB})n_B + k_{BC}n_C \\ \frac{dn_C}{dt} &= k_{CA}n_A + k_{CB}n_B - (k_{AC} + k_{BC})n_C. \end{aligned} \tag{3.2}$$

If one or several of the coefficients k_{BA} etc. vanish the case becomes trivial; we shall therefore assume that they are all $\gtrless 0$. This condition is by itself sufficient to insure finite equilibrium concentrations $\bar{n}_A$, $\bar{n}_B$, $\bar{n}_C$, which are given by the relations

$$\frac{d\bar{n}_A}{dt} = 0 = -(k_{BA} + k_{CA})\bar{n}_A + k_{AB}\bar{n}_B + k_{AC}\bar{n}_C \tag{3.3}$$

together with

$$\bar{n}_A + \bar{n}_B + \bar{n}_C = n_A + n_B + n_C = n \tag{3.4}$$

expressing the conservation of the total amount. If the equilibrium ratios $\bar{n}_A:\bar{n}_B:\bar{n}_C$ are known this implies two independent relations between the 6 coefficients k_{AB}, k_{AC}, $\cdots$ k_{CB}, leaving 4 of them free.

Here, however, the chemists are accustomed to impose a very interesting additional restriction, namely: when the equilibrium is reached each indi-

viual reaction must balance itself. They require that the transition $A \rightarrow B$ must take place just as frequently as the reverse transition $B \rightarrow A$ etc. Now if the ratios between $\bar{n}_A$, $\bar{n}_B$, and $\bar{n}_C$ are known the condition of detailed balancing imposes three relations between the k's instead of the two expressed by (3.3), namely

$$\begin{aligned} k_{BA}\bar{n}_A &= k_{AB}\bar{n}_B \\ k_{CB}\bar{n}_B &= k_{BC}\bar{n}_C \\ k_{AC}\bar{n}_C &= k_{CA}\bar{n}_A . \end{aligned} \tag{3.5}$$

These reciprocal relations are analogous to (2.4). From (3.5) we can obtain just one relation between k_{AB} etc. alone, namely

$$k_{AC}k_{CB}k_{BA} = k_{AB}k_{BC}k_{CA} .$$

This relation is not necessary for fulfilling the thermodynamic requirements; those are satisfied as soon as an equilibrium exists, and the existence of an equilibrium is secured by any set of positive values of $k_{AB} \cdots k_{CB}$. In terms of equations: (3.5) is not contained in (3.3).

Suppose that (3.5) were not fulfilled, how could the equilibrium be maintained? Besides a certain number of transitions balancing each other directly according to the scheme

$$\begin{aligned} A &\rightleftarrows B \\ B &\rightleftarrows C \\ C &\rightleftarrows A \end{aligned}$$

we should have additional transitions taking place around the cycle

$$\begin{array}{ccc} A & \searrow & \\ \uparrow & & B \\ C & \nearrow & \end{array} \tag{3.6}$$

Now the idea of an equilibrium maintained by a mechanism like (3.6) whether entirely or only in part, is not in harmony with our notion that molecular mechanics has much in common with the mechanics of ordinary conservative dynamical systems. Barring certain exceptional cases[8] which can readily be recognized and sorted out, the dynamical laws of familiar conservative systems are always reversible, that means: if the velocities of all the particles present are reversed simultaneously the particles will retrace their former paths, reversing the entire succession of configurations. We like to think that the dynamical laws which govern the world of atoms are also reversible. The information that we have about the atoms affords considerable support for this belief of ours, and we have no serious counter-indications, if any. If the dynamical laws of an isolated molecular system are reversible the kinetic theory requires that in the long run every type of motion must occur just as often as its reverse, because the congruence of the two types of motion makes them *apriori* equivalent. This implies that if we wait a long time so as to make sure of thermodynamic equilibrium, in the end every type of motion

[8] Coriolis forces, external magnetic fields (and permanent magnets). See §7.

is just as likely to occur as its reverse. One consequence of this *principle of dynamical reversibility* is the condition that when a molecule changes a certain number of times per second from the configuration A to the configuration B the *direct* reverse transition $B \rightarrow A$ must take place equally often, as expressed by (3.5).

In order to see the full analogy between the reciprocal relations (3.5) and 2.4) we must find an expression for the change in free energy involved by the chemical reactions (3.1). Assuming in accordance with the ideal mass-action formula (3.2) that the molecules A, B, and C form an ideal solution we may express the dependance of the "free energy at constant pressure" Z of n_A, n_B and n_C in the form

$$Z = Z_{min} + RT(n_A \log (n_A/\bar{n}_A) + n_B \log (n_B/\bar{n}_B) + n_C \log (n_C/\bar{n}_C)) \quad (3.7)$$

Thus

$$\delta Z_{(P,T,n)} = RT(\log (n_A/\bar{n}_A)\delta n_A + \log (n_B/\bar{n}_B)\delta n_B + \log (n_C/\bar{n}_C)\delta n_C)$$

We shall introduce the notation

$$x_A = n_A - \bar{n}_A \quad \text{etc.} \qquad (3.8)$$

and write

$$\delta Z = - X_A \delta x_A - X_B \delta x_B - X_C \delta x_C.$$

In order to obtain proportionality between the "forces" X and the displacements x we must limit ourselves to the consideration of cases where the system is nearly in equilibrium, i.e.

$$x_A << \bar{n}_A \text{ etc.}$$

Then we have

$$\begin{aligned} X_A &= - RT \log (n_A/\bar{n}_A) \sim - \frac{RT}{\bar{n}_A} x_A \\ X_B &\sim - \frac{RT}{\bar{n}_B} x_B \qquad (3.9) \\ X_C &\sim - \frac{RT}{\bar{n}_C} x_C. \end{aligned}$$

Observing (3.3) and 3.8) the Eqs. (3.2) may be written in form

$$\dot{x}_A = \frac{dx_A}{dt} = -(k_{BA} + k_{CA})x_A + k_{AB}x_{AB} + k_{AC}x_C$$

or, finally, with the aid of (3.9)

$$\begin{aligned} \dot{x}_A &= (k_{BA} + k_{CA})\frac{\bar{n}_A}{RT} X_A - \frac{k_{AB}\bar{n}_B}{RT} X_B - \frac{k_{AC}\bar{n}_C}{RT} X_C \\ \dot{x}_B &= - \frac{k_{BA}\bar{n}_A}{RT} X_A + (k_{AB} + k_{CB})\frac{\bar{n}_B}{RT} X_B - \frac{k_{BC}\bar{n}_C}{RT} X_C \qquad (3.10) \\ \dot{x}_C &= - \frac{k_{CA}\bar{n}_A}{RT} X_A - \frac{k_{CB}\bar{n}_B}{RT} X_B + (k_{AC} + k_{BC})\frac{\bar{n}_C}{RT} X_C. \end{aligned}$$

Comparing (3.10) with (2.3) the complete analogy between (3.5) and (2.4) is apparent.[9]

This comparison suggests that reciprocal relations of the type (2.4) can be derived from the principle of microscopic reversibility. It is true that in the above derivation of (3.5) we started out from a special picture; but we saw at least that this picture was not by itself sufficient to yield the reciprocal relations (3.5). The feature that simplified the consideration so much was the assumed mechanism of elementary transitions, which permitted us to apply the condition of reversibility, or "detailed balancing," to each type of transitions separately. We can already recognize the essential elements in the derivation of (1.2) (which is only another form of (2.4)) from the electron theory of metals. In those deductions it was assumed that the rates of transport processes were limited by collisions between particles whose velocities were distributed according to Maxwell's law. Now the collision is in effect a kind of transition leading from a state characterized by one pair of velocities (v_1', v_2') to another state (v_1'', v_2''). The requirement of microscopic reversibility enters through the condition that the transitions:

$$(v_1', v_2') \rightarrow (v_1'', v_2'') \text{ and } (-v_1'', -v_2'') \rightarrow (-v_1', -v_2')$$

must occur equally often when the system has reached thermodynamic equilibrium.

For a general derivation of reciprocal relations like (2.4) we should like to make no reference whatsoever to any particular type of mechanism. We understand already that any mechanism representing an irreversible process as the net resultant of many independent elementary transitions is liable to yield the expected relations; but we have to deal with many cases where no such mechanism can reasonably be assumed. For that reason we want to consider only the integral changes that are involved by the irreversible process. At the same time we want to apply our basic assumption of microscopic reversibility. There is just one possible way: We must consider the *fluctuations* in a system which has been left isolated for a length of time that is normally sufficient to secure thermodynamic equilibrium.

4. Heat Conduction and Fluctuations of the Distribution of Energy in a Crystal

We shall show in a simple concrete example how the principle of microscopic reversibility demands reciprocal relations in transport processes. The

[9] Strictly speaking, one may object that there is a difference between the two cases inasmuch as x_A, x_B, and x_C are subject to the restriction:

$$x_A + x_B + x_C = 0$$
$$\dot{x}_A + \dot{x}_B + \dot{x}_C = 0$$

(because of (3.3) and (3.8)); so that (3.10) actually contains only two independent variables. However, this only means that (3.10) is analogous to a set of equations of the type (2.3) written out for two variables J_1, J_2 instead of three, i.e., (2.1), with only one reciprocal relation (2.2). This statement may be verified by eliminating one of the variables x, say x_C, in the equations (3.7) etc. The whole complication is quite trivial, and we shall spare ourselves the trouble of going through the details of the calculation here.

consideration of fluctuations will enable us to treat the stationary thermodynamic equilibrium as the average result of transitions in different directions without any explicit assumption regarding elementary transitions. We must of course connect the fluctuations with the macroscopic laws of thermodynamics and irreversible processes by reasonable general assumptions. The principles involved are not new; they are classical theorems of statistical mechanics. To begin with, let us contrast the thermodynamic to the statistical point of view.

In thermodynamics we assume that when a system has been left isolated for a sufficient length of time it will reach a state of equilibrium, where all the visible properties of the system remain constant. The approach to equilibrium is irreversible.

The kinetic theory allows only a statistical interpretation of the second law of thermodynamics; the reversible fundamental laws of dynamics are not compatible with absolutely irreversible processes. For instance, we take the point of view that the uniform distribution of a gas within an enclosure is a stable equilibrium state simply because any other distribution is much less probable. We recognize the possibility that a gas may by some freak occurrence compress itself without external aid into one-half of the available volume, although we do not expect ever to observe such an event; the probability is exceedingly small, namely: 2^{-N}, where N is the total number of molecules present. While such large deviations from the normal are exceedingly rare smaller deviations will occur much more frequently, and the common deviations from the average number of molecules in either half of the vessel will be of the order of magnitude $(N)^{\frac{1}{2}}$.

In connection with the theory of heat conduction we shall naturally study the fluctuating deviations from the thermal equilibrium. For instance, we may follow the variations in the position of the center of gravity of the energy.[10] According to thermodynamics this point will remain at rest after thermal equilibrium has been reached. According to statistical mechanics we may expect a succession of slightly asymmetrical distributions of energy. Then the motion of the center of gravity of the distribution is a legitimate object of study.

The ordinary macroscopic laws of heat conduction relate the flow of heat to the temperature gradient at any given time, so that the distribution of energy at any one time determines all subsequent distributions. From the point of view of the kinetic theory this pre-determination cannot be interpreted as absolute; for instance, we do not expect to find an ultimate motionless and completely uniform distribution as required by the macroscopic laws. Still these laws will have a quite definite meaning in the kinetic theory as well. Suppose that we reproduce the same distribution of energy many times independently. Then the subsequent distributions will not be exactly the same in all cases, nor will the rates of change agree exactly with the macroscopic laws in each individual case; but the average rates for a large number

[10] Coordinates $\xi_1=\alpha_1/E$; $\xi_2=\alpha_2/E$, α_1 and α_2 being defined by (4.3). We must of course make an arbitrary convention about the total content of energy E.

of cases will follow definite laws, and these laws will agree exactly with the macroscopic laws for the conduction of heat.

We also expect that an asymmetric distribution of energy will be exactly the same whether it has arisen accidentally from fluctuations or has been produced purposely by means of suitable external heating and cooling. Once a given distribution of energy is present its history is immaterial, but, as we have pointed out above, the distribution that is present at any given time determines an average expectancy for the rates of the subsequent changes. In all instances this average expectancy for the rate of transport of heat is related to the momentary distribution by the ordinary macroscopic laws for the conduction of heat.

We shall consider the simplest case that is not trivial, namely: a crystal with a 3-, 4- or 6- counting axis of symmetry (x_3)

$$x_1 + ix_2 \to (x_1 + ix_2)e^{2\pi im/n} \quad (n = 3, 4 \text{ or } 6) \quad (m = 1, 2 \cdots) \tag{4.1}$$

and no other elements of symmetry except possibly a plane of symmetry perpendicular to x_3 ($x_3 \to -x_3$) and a center of symmetry ($x_1, x_2, x_3 \to -x_1, -x_2, -x_3$). The equations for the conduction of heat take the form (2.8), or

$$\begin{aligned} -TJ_1 &= \lambda_1 \partial T/dx_1 + \omega_3 \partial T/dx_2 \\ -TJ_2 &= -\omega_3 \partial T/dx_1 + \lambda_1 \partial T/dx_2 \\ -TJ_3 &= \lambda_3 \partial T/dx_3. \end{aligned} \tag{4.2}$$

Since clockwise and counterclockwise rotations are not equivalent, and $\omega_3 \gtrless 0$ and the spiral motion of heat which we mentioned in §2 are allowed by the symmetry of the crystal. However, if we may rely on the principle of microscopic reversibility, then a state of motion in any direction is equivalent to a state of motion in the opposite direction, and for that reason ω_3 must vanish. Argument and statements are admittedly incomplete. We could not reason in such a simple manner if the case were not so symmetrical, nor would the results be quite as simple. However, let us undertake a more detailed analysis.

We shall study the fluctuations of the distribution of energy in an isolated crystal. In order to take full advantage of the rotational symmetry expressed by (4.1) and (4.2) we give the external shape of the crystal rotational symmetry about the x_3 axis. The origin of our frame of reference may be at the center of gravity of the crystal; the orientation of the axes is already determined by the symmetry. We shall consider displacements of heat in the directions x_1 and x_2. We measure the asymmetry of a given distribution of heat by the moments

$$\begin{aligned} \alpha_1 &= \int \epsilon \cdot x_1 dV \\ \alpha_2 &= \int \epsilon \cdot x_2 dV \end{aligned} \tag{4.3}$$

where $\epsilon = \epsilon(x_1, x_2, x_3)$ is the local density of energy,[11] and the integration is extended over the total volume V of the crystal. The displacements α_1 and α_2 will differ a little from zero most of the time because of fluctuations; their averages will vanish

$$\bar{\alpha}_1 = \bar{\alpha}_2 = 0.$$

For reasons of symmetry the average squares of α_1 and α_2 must be equal, and displacements in the directions x_1 and x_2 will be independent

$$\overline{\alpha_1^2} = \overline{\alpha_2^2}; \quad \overline{\alpha_1\alpha_2} = 0. \tag{4.4}$$

The same displacement (α_1, α_2) of energy may be produced by different distributions of energy, and, accordingly, of temperature. However, to each value of α_1, there will correspond a certain average temperature gradient

$$\overline{\partial T/dx_1}^{\alpha_1} = -T\overline{X}_1(\alpha_1)$$

in the x_1 direction, the averaging to be extended over all cases where α_1 takes the same value, and in each case over all volume elements of the crystal. This average gradient will be proportional to α_1:

$$\overline{\partial T/dx_1}^{\alpha_1} = -T\overline{X}_1(\alpha_1) = TC\alpha_1.$$

In a similar manner

$$\overline{\partial T/dx_2}^{\alpha_2} = -T\overline{X}_2(\alpha_2) = TC\alpha_2$$

and if we consider a displacement (α_1, α_2) in an arbitrary direction:

$$\begin{aligned} -T\overline{X}_1(\alpha_1, \alpha_2) &= TC\alpha_1 \\ -T\overline{X}_2(\alpha_1, \alpha_2) &= TC\alpha_2 \end{aligned} \tag{4.5}$$

The factor C can be calculated on the basis of the general theory of fluctuations.[12] In this particular case we shall be content to know that α_1 causes no temperature gradient in the x_2 direction, and *vice versa*, in spite of the fact that rotations in opposite directions in the x_1, x_2 plane are not equivalent. The reason is that in questions regarding the distribution the anisotropy of the crystal is immaterial anyway, and only the external boundary of the crystal is important, because all the volume elements of a homogeneous crystal are equivalent irrespective of location or mutual connections. The anisotropy becomes important as soon as one considers the *rate of exchange* of energy.

The temperature gradient determines the average rate of transport of heat according to (4.2)

$$\begin{aligned} \bar{J}_1(\alpha_1, \alpha_2) &= \lambda_1\overline{X}_1(\alpha_1, \alpha_2) + \omega_3\overline{X}_2(\alpha_1, \alpha_2) = -\lambda_1C\alpha_1 - \omega_3C\alpha_2 \\ \bar{J}_2(\alpha_1, \alpha_2) &= -\omega_3\overline{X}_1(\alpha_1, \alpha_2) + \lambda_1\overline{X}_2(\alpha_1, \alpha_2) = \omega_3C\alpha_1 - \lambda_1C\alpha_2. \end{aligned} \tag{4.6}$$

[11] Strictly speaking, one may identify heat with energy only when the crystal has no thermal expansion in any direction. In general heat must be defined as energy less work of deformation and expansion. This complicates the discussion slightly without changing the results; the symmetry conditions (4.4) and (4.5) remain valid.

[12] Einstein, Ann. d. Physik **33**, 1275 (1910).

Finally, if V is the volume, then $V\bar{J}_1$ is the total rate of transport of heat in the x_1 direction:

$$d\alpha_1/dt = V\bar{J}_1$$

and we obtain

$$\begin{aligned} \overline{d\alpha_1/dt} &= -\lambda_1 VC\alpha_1 - \omega_3 VC\alpha_2 \\ \overline{d\alpha_2/dt} &= \omega_3 VC\alpha_1 - \lambda_1 VC\alpha_2. \end{aligned} \tag{4.7}$$

Suppose now that we watch our crystal for a great length of time. Whenever the displacement of energy in the x_1 direction happens to be $\alpha_1 = \alpha_1'$ we note down the displacement α_2 in the x_2 direction Δt seconds later. The average of a great number of such observations we shall denote by

$$\bar{\alpha}_2(\Delta t, \alpha_1').$$

For reasons of symmetry

$$\bar{\alpha}_2(0, \alpha_1') = 0$$

because this average does not depend on the rate of transport, but only on the relative probabilities of different distributions of energy (simultaneous values of α_1 and α_2). The average change of α_2 in a time Δt subsequent to distributions for which $\alpha_1 = \alpha_1'$ is therefore

$$\bar{\alpha}_2(\Delta t, \alpha_1') - \bar{\alpha}_2(0, \alpha_1') = \bar{\alpha}_2(\Delta t, \alpha_1').$$

If Δt is sufficiently small we can calculate this change from (4.7):

$$\bar{\alpha}_2(\Delta t, \alpha_1') = \bar{\alpha}_2(\Delta t, \alpha_1') - \bar{\alpha}_2(0, \alpha_1') = \overline{d\alpha_2/dt}^{\alpha_1'} \cdot \Delta t = \omega_3 VC\alpha_1' \Delta t \tag{4.8}$$

Now we can calculate the average product

$$\overline{\alpha_1(t)\alpha_2(t + \Delta t)} = \lim_{t'' \to \infty} \frac{1}{t'' - t'} \int_{t=t'}^{t=t''} \alpha_1(t)\alpha_2(t + \Delta t)dt$$

Obviously:

$$\overline{\alpha_1(t)\alpha_2(t + \Delta t)} = \overline{\alpha_1' \bar{\alpha}_2(\Delta t, \alpha_1')} = \omega_3 VC\overline{\alpha_1^2}\Delta t. \tag{4.9a}$$

In a similar manner, or directly from (4.9a) by taking into account the rotational symmetry (4.1) of the crystal we obtain:

$$\overline{\alpha_2(t)\alpha_1(t + \Delta t)} = -\omega_3 VC\overline{\alpha_1^2}\Delta t = -\omega_3 VC\overline{\alpha_2^2}\Delta t. \tag{4.9b}$$

Here

$$\overline{\alpha_1^2} = \overline{\alpha_2^2}$$

The principle of microscopic reversibility demands that a displacement $\alpha_1 = \alpha_1'$ of energy in the x_1 direction, followed τ seconds later by a displacement $\alpha_2 = \alpha_2''$ in the x_2 direction, must occur just as often as $\alpha_2 = \alpha_2''$, followed τ seconds later by $\alpha_1 = \alpha_1'$. Consequently

$$\overline{\alpha_1(t)\alpha_2(t + \tau)} = \overline{\alpha_2(t)\alpha_1(t + \tau)} \tag{4.10}$$

where τ may have any value, for example $\tau = \Delta t$. Comparing with (4.9a, b) we have

$$\omega_3 = 0 \tag{4.11}$$

in accordance with Voigt's experimental result,[7] the simplest example of a reciprocal relation in irreversible processes.

Here we have taken a little more out of the principle of microscopic reversibility than we did in section 3 with the assertion that transitions between two (classes of) configurations A and B should take place equally often in the directions $A \rightarrow B$ and $B \rightarrow A$ in a given time τ. Above we have discussed transitions between different distributions of energy. We must expect that the energy will depend not only on the configuration of elementary particles, but also on their velocities; we do not know exactly how. However, assuming microscopic reversibility, the energy must depend on the velocities in such a manner that every type of motion has the same energy as its reverse; otherwise a "reverse" energy would exist, different from the ordinary energy but with similar properties of conservation, and we should not know the energy as a unique function of the state of the system. If the energy can be localized so that we can speak about distributions of energy in space, the distribution of energy must be the same for corresponding phases of direct and reverse motion, or similar discrepancies would arise. Since, by hypothesis, direct and reverse motion of every conceivable type occur pairwise equally often, if A and B be two distributions of energy, the transitions $A \rightarrow B$ and $B \rightarrow A$ (in time intervals of a given length τ) must occur equally often.

We shall comment on another question regarding the premises of the derivation, although the substance of a satisfactory answer is known from a famous discussion between Loschmidt and Boltzmann.[13] We have assumed microscopic reversibility, and at the same time we have assumed that the average decay of fluctuations will obey the ordinary laws of heat conduction. Already an apparent contradiction occurs when we consider the simpler case of heat conduction in one dimension. Let α be a displacement of heat, then:

$$\dot{\bar{\alpha}} = d\bar{\alpha}/dt = -K\alpha. \tag{4.12}$$

Microscopic reversibility requires

$$\bar{\alpha}(\tau, \alpha') = \bar{\alpha}(-\tau, \alpha'). \tag{4.13}$$

Clearly

$$\dot{\alpha}(\tau, \alpha') = -\dot{\alpha}(-\tau, \alpha')$$

and:

$$\dot{\bar{\alpha}}(0, \alpha') = -\dot{\alpha}(0, \alpha') = 0.$$

According to the ordinary laws for conduction of heat $\bar{\alpha}$ decreases for positive τ (if $\alpha' > 0$). According to (4.13), then, $\bar{\alpha}$ increases for negative τ (average growth of fluctuations), and $\dot{\bar{\alpha}} = 0$ for $\tau = 0$. It may appear somewhat startling

[13] See P. and T. Ehrenfest, Enz. d. math. Wiss. IV. **32.**

that we apply (4.12) to fluctuations only for $\tau > 0$, and not for $\tau \leqq 0$. Yet in this there is no logical contradiction—we have stated bluntly and honestly that α has a discontinuity for $\tau = 0$—but such a statement disappoints our expectation of continuity in nature. However, the objection is removed when we recognize that (4.12) is only an approximate description of the process of conduction, neglecting the time needed for acceleration of the heat flow. This time τ_0 is probably rather small, e.g. in gases it ought to be of the same order of magnitude as the average time spent by a molecule between two collisions. For practical purposes the time-lag can be neglected in all cases of heat conduction that are likely to be studied, and this approximation is always involved in the formulation of laws like (4.12), (4.7) and (4.2). Even the differential form (e.g. (4.8)) of these equations is justified; because we can usually choose a time Δt such that:

$$1 \gg K\Delta t \gg K\tau_0.$$

Then following $t = \tau_0$, which is practically the same as $t = 0$, we have a time interval $\Delta t \gg \tau_0$ in which (by (4.12)) α and therefore $d\alpha/dt$ are sensibly constant. We may also recall that the time needed for equalization of temperature in a body is proportional to the square of its linear dimensions l, i.e.:

$$K \sim 1/l^2.$$

In gases $K\tau_0$ should be of the order l^2/Λ^2, where Λ is the mean free path. The ordinary laws for conduction of heat are therefore asymptotic laws for $l \gg \Lambda$.

The preceding considerations leading to (4.11) are easily extended to the more general case of heat conduction in a crystal of arbitrary symmetry. The phenomenological equations have the form

$$\begin{aligned} J_1 &= L_{11}X_1 + L_{12}X_2 + L_{13}X_3 \\ J_2 &= L_{21}X_1 + L_{22}X_2 + L_{23}X_3 \\ J_3 &= L_{31}X_1 + L_{32}X_2 + L_{33}X_3 \end{aligned} \tag{2.3}$$

where

$$TX_1 = -\partial T/dx_1;\ TX_2 = -\partial T/dx_2;\ TX_3 = -\partial T/dx_3. \tag{4.14}$$

We shall derive the reciprocal relations:

$$L_{12} = L_{21};\ L_{23} = L_{32};\ L_{31} = L_{13}. \tag{2.4}$$

We chose the external shape of our crystal spherical. Since the anisotropy of the crystal has nothing to do with the distribution of heat the arguments leading to (4.4) and (4.5) apply equally well in this case, and we obtain

$$\overline{\alpha_1^2} = \overline{\alpha_2^2} = \overline{\alpha_3^2};\ \overline{\alpha_1\alpha_2} = \overline{\alpha_2\alpha_3} = \overline{\alpha_3\alpha_1} = 0 \tag{4.15}$$

$$\begin{aligned} -\overline{X}_1(\alpha_1, \alpha_2, \alpha_3) &= C\alpha_1 \\ -\overline{X}_2(\alpha_1, \alpha_2, \alpha_3) &= C\alpha_2 \\ -\overline{X}_3(\alpha_1, \alpha_2, \alpha_3) &= C\alpha_3. \end{aligned}$$

Instead of (4.6) and (4.7) we find

$$\overline{J_1}(\alpha_1, \alpha_2, \alpha_3) = -L_{11}C\alpha_1 - L_{12}C\alpha_2 - L_{13}C\alpha_3, \text{ etc.}$$
$$\overline{d\alpha_1/dt} = -L_{11}\Gamma C\alpha_1 - L_{12}\Gamma C\alpha_2 - L_{13}\Gamma C\alpha_3, \text{ etc.}$$

The analogy of (4.8) becomes

$$\overline{\alpha_2}(\Delta t, \alpha_1') = \overline{d\alpha_2/dt}^{\alpha_1'}\Delta t = -L_{21}\Gamma C\alpha_1'\Delta t$$

and we have in the place of (4.9)

$$\overline{\alpha_1(t)\alpha_2(t+\Delta t)} = \overline{\alpha_1'\bar{\alpha}_2(\Delta t, \alpha_1')} = -L_{21}\Gamma C\overline{\alpha_1^2}\Delta t \tag{4.16a}$$

Likewise

$$\overline{\alpha_2(t)\alpha_1(t+\Delta t)} = -L_{12}\Gamma C\overline{\alpha_2^2}\Delta t \tag{4.16b}$$

Microscopic reversibility (4.10) requires

$$\overline{\alpha_1(t)\alpha_2(t+\Delta t)} = \overline{\alpha_2(t)\alpha_1(t+\Delta t)}.$$

Comparison with (4.16a, b) and (4.15) yields the generalization of (4.11)

$$L_{12} = L_{21}.$$

The other two equations in (2.4) are obviously derived in the same way.

5. The Principle of the Least Dissipation of Energy

Like the reciprocal relations of mechanics and thermodynamics the relations (2.4) can be expressed in terms of a potential, and permit the formulation of a variation principle. As a preliminary we re-write (2.3) and (4.14) expressing the "forces" X by the "velocities" J:

$$\begin{aligned} -\frac{1}{T}\frac{\partial T}{dx_1} &= X_1 = R_{11}J_1 + R_{12}J_2 + R_{13}J_3 \\ -\frac{1}{T}\frac{\partial T}{dx_2} &= X_2 = R_{21}J_1 + R_{22}J_2 + R_{23}J_3 \\ -\frac{1}{T}\frac{\partial T}{dx_3} &= X_3 = R_{31}J_1 + R_{32}J_2 + R_{33}J_3 \end{aligned} \tag{5.1}$$

where $R_{11} \cdots R_{33}$ are connected with $L_{11} \cdots L_{33}$ in (2.3) by the well known relations

$$\sum_{m=1}^{3} L_{im}R_{mk} = \sum_{m=1}^{3} R_{im}L_{mk} = \delta_{ik} = \begin{cases} 1 & (i = k) \\ 0 & (i \gtrless k) \end{cases}$$

and the reciprocal relations (2.4) are equivalent to:

$$R_{12} = R_{21};\ R_{13} = R_{31};\ R_{23} = R_{32}. \tag{5.2}$$

Here, if we write:

$$2\phi(J, J) \equiv \frac{1}{T}\sum_{i,k} R_{ik}J_iJ_k \tag{5.3}$$

the relations (5.1) may be written:

$$\frac{1}{T}X_k = \frac{\partial}{dx_k}\left(\frac{1}{T}\right) = \frac{\partial\phi(J, J)}{dJ_k}. \tag{5.4}$$

We also observe that:

$$2T\phi(J, J) \equiv \sum_{k=1}^{3} J_k T\partial\phi/dJ_k = J_1X_1 + J_2X_2 + J_3X_3 \tag{5.5}$$

The function $\phi(J, J)$ we shall call the *dissipation-function*. It is a direct generalization of a function which was introduced by Lord Rayleigh[14] and applied to mutual interaction of frictional forces; it plays the part of a *potential* for such forces. Actually Lord Rayleigh used the function $F(J, J) = T\phi(J, J)$ and called F the dissipation-function; for our purposes we shall find the function ϕ more generally useful. As we shall see immediately, $2\phi(J, J)$ equals the rate of production of entropy due to heat flow across a volume element (of unit size), so that $2T\phi = 2F$ equals the rate of "dissipation" of free energy.

The rate of local accumulation of heat equals

$$Tds/dt = -\operatorname{div} J = -\partial J_1/dx_1 - \partial J_2/dx_2 - \partial J_3/dx_3 \tag{5.6}$$

writing s for the local entropy density, and the total rate of increase of the entropy S equals

$$dS/dt = \int (ds/dt)dV = \int\left(-\frac{1}{T}\operatorname{div} J\right)dV.$$

By Green's theorem:

$$\int\int\int (-\operatorname{div} J)\frac{1}{T}\,dV + \int\int\frac{J_n}{T}\,d\Omega = \int\int\int\left(J, \operatorname{grad}\frac{1}{T}\right)dV$$

$$= \int\int\int\left(J_1\frac{\partial}{dx_1}\left(\frac{1}{T}\right) + J_2\frac{\partial}{dx_2}\left(\frac{1}{T}\right) + J_3\frac{\partial}{dx_3}\left(\frac{1}{T}\right)\right)dV$$

where the double integral on the left is extended over the boundary Ω of the body in question, and J_n is the normal component of the heat flow at the boundary. If we write

$$\dot{S}^*(J_n) \equiv \int\int (J_n/T)d\Omega \tag{5.7}$$

for the entropy given off to the surroundings, and

$$\dot{S}(J) \equiv \int\int\int\left(-\frac{1}{T}\operatorname{div} J\right)dV \tag{5.8}$$

[14] Lord Rayleigh, Proc. Math. Soc. London **4**, 357, [363], (1873). Theory of Sound, (London, MacMillan Co., 1st ed. 1877), Vol. I, p. 78; (2d ed. 1894), Vol. I, p. 102.

for the entropy change of the system proper, we have:

$$\dot{S}(J) + \dot{S}^*(J_n) \equiv \int \left(J, \text{grad } \frac{1}{T}\right) dV \equiv \int \sum_k J_k \frac{\partial}{dx_k}\left(\frac{1}{T}\right) dV$$
$$\equiv \int \frac{1}{T} \sum_k J_k X_k dV \tag{5.9}$$

(observing (4.14)). Now, by (5.4) and (5.5)

$$\int \sum_k J_k \frac{\partial}{dx_k}\left(\frac{1}{T}\right) dV = \int \sum_k J_k \frac{\partial \phi(J, J)}{dJ_k} dV = \int 2\phi(J, J) dV.$$

Inserting this in (5.9) we find

$$2\Phi(J, J) \equiv 2 \int \phi(J, J) dV = \dot{S}(J) + \dot{S}^*(J_n). \tag{5.10}$$

Now we shall show that the relations (5.4) are equivalent to the *variation principle*

$$\dot{S}(J) + \dot{S}^*(J_n) - \Phi(J, J) = \text{maximum} \tag{5.11}$$

with the conventions that the temperature distribution $T(x_1, x_2, x_3)$ is prescribed, the flow $J(x_1, x_2, x_3)$ is varied, and the functions $\dot{S}$, $\dot{S}^*$ and Φ are defined by (5.7), (5.8) and (5.10), respectively (reading ($\equiv$), but not ($=$): "identical in J"). Observing (5.9) we have

$$\delta[\dot{S}(J) + \dot{S}^*(J_n) - \Phi(J, J)]$$
$$= \delta \int \left[\sum_k J_k \frac{\partial}{dx_k}\left(\frac{1}{T}\right) - \phi(J, J) \right] dV$$
$$= \int \sum_k \left[\frac{\partial}{dx_k}\left(\frac{1}{T}\right) - \frac{\partial}{dJ_k} \phi(J, J) \right] \delta J_k dV$$

so that (5.4) is clearly equivalent to

$$\delta[\dot{S}(J) + \dot{S}^*(J_n) - \Phi(J, J)] = 0.$$

Here, since $\dot{S}$ and $\dot{S}^*$ are linear functionals of J, and Φ is a homogeneous quadratic functional, the expression in the brackets can have only one extremum. This extremum is a maximum because $\Phi(J, J)$ must be positive-definite (otherwise (5.10) would not agree with the second law of thermodynamics).

If the boundary is isolated the restriction

$$J_n = 0 \tag{5.12}$$

enters, and, since then $\dot{S}^*(J_n)$ vanishes

$$\dot{S}(J) - \Phi(J, J) = \text{maximum}. \tag{5.13}$$

Thus the vector field J of the heat flow is described by the condition that the rate of increase of the entropy, less the dissipation-function, be a maximum.

In applications the difference between the formulations (5.11) and (5.13) is trivial. From a fundamental point of view (5.13) has some merit of greater simplicity because it applies to an isolated system, and is thus more directly connected with the theory of fluctuations. Above we have demonstrated (5.13) for anisotropic heat conduction. A more general theorem applying to all transport processes (conduction of electricity and heat, and diffusion) can be derived in a similar manner, only it is then necessary to make full use of the general theory of fluctuations, involving Boltzmann's classical relation between entropy S and probability W

$$S = k \log W + \text{const}.$$

This general development will be deferred to a following communication.

6. Stationary Flow and Quasi-Thermodynamics

A brief discussion of the conditions for stationary flow of heat through an anisotropic body will bring out an interesting simple consequence of (5.11) and throw light on the connection with previous quasi-thermodynamic derivations of reciprocal relations in irreversible processes.

The condition for stationary flow of heat is

$$\text{div } \boldsymbol{J} = \partial J_1/dx_1 + \partial J_2/dx_2 + \partial J_3/dx_3 = 0 \tag{6.1}$$

for the interior of the body under consideration. No heat is accumulated in the interior, so that $\dot{S}(J) = 0$. Thus (5.11) becomes:

$$\dot{S}^*(J_n) - \Phi(J, J) = \text{maximum} \tag{6.2}$$

Eqs. (6.1) and (6.2) determine the field of flow J as well as the temperatures in the interior when the temperatures at the boundary are prescribed. (An eventual dependence of $\phi(J, J)$ on the temperature should be ignored in carrying out the variation: $\delta\phi(J, J) = \Sigma(\partial\phi/dJ_k)\delta J_k$). In this case, where $\dot{S}(J) = 0$, (5.10) becomes

$$\dot{S}^*(J_n) = 2\Phi(J, J) \tag{6.3}$$

and we have

$$2(\dot{S}^*(J_n) - \Phi(J, J)) = \dot{S}^*(J_n).$$

We may therefore state (6.2) in the alternative form

$$\dot{S}^*(J_n) = \text{maximum} \tag{6.4}$$

with the restrictions (6.1) and (6.3).

Now let us consider the effect of obstacles to the heat flow, like cracks in the crystal, introducing restrictions of the type:

$$J_n' = 0$$

for the changed heat flow J' at certain interior surfaces. Since the field J of the original heat flow made $\dot{S}^*(J_n)$ a maximum under restrictions that are also imposed on J', we must have

$$\dot{S}^*(J_n) \geqq \dot{S}^*(J_n') \tag{6.5}$$

Restrictions can only decrease the rate of production of entropy, or cause no change.

Assumptions of the type (6.5) are involved in all quasi-thermodynamic derivations proposed by earlier writers for reciprocal relations in irreversible processes. As good an example as any is Thomson's case (1.1), where J_1 is the electrical current and J_2 the heat flow (in the same direction). We maintain a constant temperature gradient $-TX_2$, while X_1 may be varied. The restriction: $J_1 = 0$ may be imposed by breaking the electric circuit. The rate of production of entropy equals

$$\dot{S}(J) + \dot{S}^*(J_n) = (V/T)(X_1J_1 + X_2J_2)$$

(cf. (5.9)). With the aid of (1.1) we transform this relation into:

$$T(\dot{S}(J) + \dot{S}^*(J_n)) = (V/R_{22})\left[X_2^2 + (R_{12} - R_{21})X_2J_1 + (R_{11}R_{22} - R_{12}R_{21})J_1^2\right].$$

Here, if we assume that the restriction

$$J_1 = 0$$

makes $\dot{S}+\dot{S}^*$ a minimum for given X_2 (cf. (6.5)), we find

$$R_{12} - R_{21} = 0. \tag{1.2}$$

In conclusion, let us describe the case which has given name to the "principle of the least dissipation of energy." The flow of heat J_n across all sections of the boundary Ω is prescribed, and the condition

$$\int J_n d\Omega = 0$$

is fulfilled. Then $\dot{S}^*(J_n)$ in (6.2) is prescribed, and the condition for stationary flow reduces to

$$\Phi(J, J) = \text{minimum} \tag{6.6}$$

subject to the restrictions:

$$J_n \text{ prescribed} \tag{6.7}$$

$$\operatorname{div} \boldsymbol{J} = 0. \tag{6.1}$$

These conditions determine J, and the temperatures are determined everywhere if known at one point.

7. Non-Reversible Systems

A dynamical system is reversible as long as the (mechanical) forces depend only on the coordinates or, if they depend on the velocities as well, are even functions of these. We know *conservative* systems which do not fulfill this condition. (i) An electric charge moving in a magnetic field is deflected by a force proportional to the product of charge and velocity. (ii) Relative to a rotating frame of reference a free particle moves as if it were subject to a transverse force proportional to the product of mass and velocity (Coriolis force) besides the centrifugal force.

When magnetic forces and Coriolis forces destroy the reversibility of macroscopic motion we must expect that the microscopic motion will fare no better. The reciprocal relations (2.4) and their equivalent, the principle of the least dissipation of energy (5.11) are derived from the assumption of microscopic reversibility. We may expect that these relations will break down in cases where magnetic or Coriolis forces are acting, and they do. The influence of Coriolis forces on heat conduction is presumably small and not easily studied; but magnetic fields are known to modify the relation between heat flow and temperature gradient in metals. In an isotropic body, the simplest case, the temperature gradient has the same direction as the heat flow as long as no magnetic field is present. However, if a transverse magnetic field is applied the temperature gradient will have a component in the third direction perpendicular to flow and field. The direction of the temperature gradient is rotated with respect to the heat flow, about an axis parallel to the magnetic field. This phenomenon is known as the Righi-Leduc effect. If a circular metal plate is placed perpendicular to the magnetic field, heated in the middle and cooled at the edge, the heat will flow outward in spirals. The equations of the heat flow take the form (2.8), or rather

$$\begin{aligned} J_1 &= \lambda X_1 + \omega X_2 \\ J_2 &= -\omega X_1 + \lambda X_2 \\ J_3 &= \lambda X_3 \end{aligned} \tag{7.1}$$

where ω is proportional to the intensity of the magnetic field (for weak fields); the field is thought parallel to the x_3 direction. The principle of the least dissipation of energy is no longer valid; radial cracks in the plate will *increase* the rate of radial transport of heat for a given temperature gradient.

More familiar than the Righi-Leduc effect is perhaps the Hall effect. When a constant current is flowing through a metallic conductor a transverse magnetic field causes an e.m.f. perpendicular to both. Eqs. (7.1) describe the isotropic case if J_1, J_2, J_3, denote the components of the current and X_1, X_2, X_3 the components of the electric field.

In the presence of a magnetic field the principle of microscopic reversibility may be applied in a modified form: The entire motion may be reversed by reversing the magnetic field together with the velocities of all the particles composing a dynamical system. Eqs. (7.1) are in accord with this requirement.

An analogous effect of Coriolis forces is known in hydrodynamics. The principle of the least dissipation of energy applies to the motion of very viscous fluids (Stokes' limiting case) as long as the motion is not referred to a rotating frame of reference.

THE DIELECTRIC CONSTANT AND ELECTRIC MOMENT OF SOME AMINES

By P. N. Ghosh and T. P. Chatterjee
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(Received January 6, 1931)

Abstract

By using a heterodyne null-beat arrangement, the electric moments have been calculated and the following results obtained: methyl amine, $A=1.37\times10^{-3}$, $\mu=0.99\times10^{-18}$; dimethyl amine, $A=1.22\times10^{-3}$; $\mu=0.90\times10^{-18}$; trimethyl amine, $A=1.19\times10^{-3}$; $\mu=0.82\times10^{-18}$; ethylamine, $A=2.37\times10^{-3}$; $\mu=0.99\times10^{-18}$; diethyl amine, $A=2.59\times10^{-3}$; $\mu=0.90\times10^{-18}$; and triethyl amine, $A=2.90\times10^{-3}$; $\mu=0.82\times10^{-18}$.

Introduction

IT HAS been found by several investigators that the dipole moment for a series of homologues is sensibly constant and is the property of a polar group present in them. For the primary alcohols[1] such a relationship has been obtained. The halogen-derivatives[2] of methane and ethane also support this view. Hojen-dahl[3] has tested the above hypothesis in many other cases. On the basis of certain assumptions, he has calculated the dipole-moment from the data of Pohrt[4] who had used a bridge method to determine the dielectric constants of vapors at a standard temperature and at varying pressures. It was, however, found from his calculations, that the amines do require a more careful study and thus form the object of the present investigation.

Experimental

The apparatus used was the heterodyne null-beat arrangement described by Mahanti in a recent paper.[2] The same procedure was followed for the measurements presented in this paper.

The electric moments have been calculated from the relation

$$\mu^2 = 1.208 \times 10^{-36} B, \tag{1}$$

which has been deduced from the Debye equation.

Discussion

It is evident from Table II that the dipole-moments of the methyl and ethyl amines are equal in magnitude while those of dimethyl and diethyl amines are among themselves equal. The dipole-moments of the trimethyl

[1] Mahanti and Das Gupta, Ind. Jour. Phys. **3**, 467 (1929); J. B. Miles, Phys. Rev. **34**, 964 (1929).

[2] Mahanti, Phys. Zeits. **31**, 546 (1930).

[3] K. Hojendahl, Dissertation, Copenhagen, 1928.

[4] Pohrt, Ann. d. Physik **42**, 569 (1913).

TABLE I.

Compound	Temp. in Abs. scale	Press. in mm of mercury	$(\epsilon-1)$ at the observed Press.	$\frac{(\epsilon-1)P_0T}{PT_0}$	$\frac{(\epsilon-1)P_0T^2}{PT_0}$
Methyl amine $(CH_3)NH_2$	296.2	110	0.0005586	0.004187	
		109	0.0005586	0.004226	1.246
		110	0.000561	0.004206	
	317.13	181	0.0008233	0.004015	
		126	0.0005709	0.003998	1.267
		248	0.001113	0.003969	
	332.4	187	0.0007812	0.003866	
		187	0.0007859	0.00389	1.287
		188	0.0007865	0.00387	
	349.5	180	0.000688	0.003718	
		105	0.0004062	0.003763	1.306
		152	0.0005834	0.003735	
	362.2	284	0.0006676	0.003658	
		173	0.0006328	0.003688	1.328
		171	0.0006201	0.003656	
Dimethyl amine $(CH_3)_2NH$	296.2	92	0.0003844	0.003445	
		82	0.0003455	0.003475	1.023
		66	0.0002759	0.003448	
	316.5	103	0.0003943	0.003296	
		114	0.0004257	0.003292	1.042
		112	0.0004184	0.003292	
		118	0.0004425	0.003304	
		114	0.0004281	0.003309	
	331.1	93	0.0003285	0.003251	
		101	0.0003433	0.003195	1.066
		113	0.0003943	0.003215	
	360.5	135	0.0004985	0.003037	
		176	0.0005353	0.003052	1.101
		112	0.000343	0.003076	
Trimethyl amine $(CH_3)_2N$	294.6	97	0.0003583	0.003027	
		97	0.0003608	0.003049	.8986
		88	0.0003266	0.003043	
		88	0.0003307	0.003083	
	309.2	85	0.0002985	0.003019	
		83	0.0002874	0.00298	.9255
		83	0.0002874	0.00298	
	324.53	170	0.0005473	0.002908	
		92	0.000295	0.002897	.9419
		130	0.0004182	0.002906	
	364.4	143	0.0003868	0.002687	
		114	0.0003142	0.002796	.9986
		146	0.0003941	0.002739	
Ethyl amine $(C_2H_5)NH_2$	294.5	65	0.0004061	0.005121	
		79	0.0004844	0.005142	1.511
		77	0.0004818	0.005129	
	300.8	55	0.0003384	0.005150	
		52	0.0003168	0.005100	1.54
		45	0.0002757	0.005129	
	315.3	67	0.0003796	0.004973	
		59	0.0003408	0.005068	1.582
	332.7	78	0.0004085	0.00485	
		76	0.0003949	0.004809	1.61
		75	0.0003941	0.004865	
	344.2	83	0.0004184	0.004829	
		81	0.0004061	0.004805	1.66
		81	0.0004085	0.004833	

TABLE I (*Continued*).

Compound	Temp. in Abs. scale	Press. in mm of mercury	$(\epsilon-1)$ at the observed Press.	$\frac{(\epsilon-1)P_0T}{PT_0}$	$\frac{(\epsilon-1)P_0T^2}{PT_0}$
Diethyl amine $(C_2H_5)_2NH$	297.2	124	0.0007259	0.004844	1.44
		124	0.0007259	0.004844	
	312.1	116	0.0006328	0.004728	
		117	0.0006353	0.004817	1.477
		104	0.0005685	0.004749	
	303.55	112	0.0006406	0.004833	
		97	0.0005538	0.004821	1.463
		92	0.0005238	0.004809	
	367.3	113	0.000486	0.004399	
		104	0.0004416	0.004346	1.604
		133	0.0005663	0.004354	
Triethyl amine $(C_2H_5)_3N$	297.6	42	0.0002471	0.004874	
		46	0.000271	0.004879	1.451
	304.65	38	0.0002162	0.004821	
		37	0.0002136	0.004897	1.481
		43	0.0002471	0.004872	
	315.5	46	0.0002518	0.004799	
		39	0.0002113	0.00476	
		30	0.000164	0.004799	1.509
		38	0.0002066	0.004776	
		38	0.0002066	0.004776	
	343.3	33	0.0001592	0.00461	
		37	0.0001781	0.004602	1.581
		37	0.0001781	0.004602	
	377.2	40	0.0001685	0.004424	
		41	0.0001733	0.004437	1.681
		42	0.0001805	0.004512	

and the triethyl amines present a similar result. Thus in the case of the n-amines, the polar group (NH_2) is mainly responsible for the development of the dipole-moment in the molecule. Similarly the (NH) group in the diamines and the (N) radicle in the triamines give rise to dipole moments in the respective molecules.

TABLE II.

Compound	A	B	$\mu\times10^{18}$	Calculated values of Hojendahl
Methyl amine	0.00137	0.826	0.99	1.31
Dimethyl amine	0.00122	0.675	0.90	1.05
Trimethyl amine	0.00110	0.560	0.82	—
Ethyl amine	0.00237	0.826	0.99	1.31
Diethyl amine	0.00259	0.675	0.90	0.94
Triethyl amine	0.00290	0.560	0.82	0.76

Table II also indicates that the dielectric constant increases with the boiling points of the compounds as is usually expected. The only exception is found in the case of methyl amine.

It is also interesting to note that Venkateswaran and Bhagavantham[5] have found a Raman line arising from a frequency of 3300 cm^{-1} (approx.) present in both methyl and ethyl amines, and have attributed this to the N-H linkage. This line, is however, absent in the spectrum of triethylamine.

[5] Venkateswaran and S. Bhagavantam, Ind. Jour. Phys. **5**, 129 (1930).

VARIATIONS WITH TEMPERATURE AND FREQUENCY OF DIELECTRIC LOSS IN A VISCOUS, MINERAL, INSULATING OIL

By Hubert H. Race

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(Received December 29, 1930)

Abstract

Debye's theory of polar molecules has been extended to give simple expressions for conditions of maximum loss per cycle in terms of equivalent circuit bridge or substitution measurements. The *dielectric loss* in a good grade of viscous mineral insulating oil has been separated into two components; one resulting from conduction, and the other showing characteristics with frequency and temperature qualitatively explained on the basis of the presence of polar molecules in the oil. A quantitative check shows the order of magnitude of this second loss to be the same as that which would be predicted by Debye's theory. The experimental curve shows a wider frequency response than the theoretical curve, indicating that the simple theory is not sufficient to account for the observed data. This may result from the presence of polar molecules of many different sizes giving an average response rather than molecules of one size only, as assumed in the theory. The size of the polar molecules necessary to give the observed effects was calculated from Deybe's theory and found to be of the right order of magnitude. Data taken over a wide range of frequency and temperature indicate the danger in drawing conclusions as to the characteristics of a material from data taken for limited ranges of experimental conditions. The curves show that either inincreasing or decreasing *power factor* can be obtained as a function of either frequency or temperature for certain narrow limits of experimental conditions. The dielectric loss in good commercial mineral insulating oils at power frequencies and operating temperatures results from conduction only, the contribution of polar molecules to the loss being negligible. Before a definite statement is made regarding the mechanism of the observed loss, studies should be made to determine whether a satisfactory theory can be developed which is based only on the motion of charged particles in a viscous medium.

Introduction

THE object of this investigation is the experimental and theoretical study of the changes of the electrical characteristics of a viscous insulating oil, such as is used in "solid type" cables, with changes in temperature and in frequency of the applied alternating potential. The data reported in this paper have been collected at intervals during the past eighteen months. Previous tests have shown that, under certain conditions, the d.c. conductivity and the equivalent parallel a.c. conductivity calculated from 1000 cycle bridge measurements, are identical.* Therefore, the ranges of frequency and temperature were extended to determine under what conditions this agreement fails. The work of Kitchin and Müller[1] indicated the possibility of explaining

* These tests are reported in a paper on "Some Electrical Characteristics of Cable Oils," which has been submitted for publication in the A.I.E.E. Journal.

[1] D. W. Kitchin and Hans Müller, Phys. Rev. **32**, 979 (1928).

variations in dielectric loss with frequency and temperature in terms of Debye's theory of polar molecules. The desire to check this theory offered another incentive in making the experiments reported in this paper.

The resulting data show characteristics qualitatively similar to those predicted by Debye's theory of polar molecules. A quantitative check was therefore made and found to be of the right order of magnitude.

Apparatus and Procedure

1. *Testing cells.*—For most of the measurements reported in this paper, the cell shown in Fig. 1 was used. The two concentric cylinders are made of a steel alloy containing 18 percent chromium and 8 percent nickel. This alloy is not attacked by hot oil and has a very small catalytic effect on the oil. The inner cylinder (1) is hollow with hemispherical ends welded on, using an atomic hydrogen flame, thereby making an oil-tight joint and completely seal-

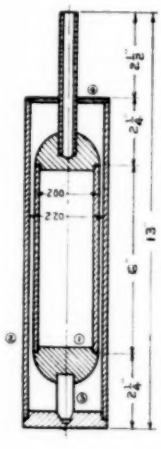


Fig. 1. Oil resistivity cell.

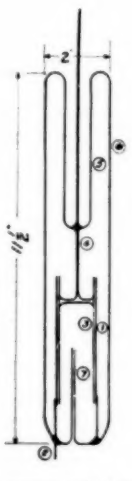


Fig. 2. Vacuum cell for electrical measurements of insulating oils.

ing the interior. The bottom of the outer cylinder (2) has a central conical hole into which the fused quartz post (3) of the inner cylinder fits. The inner electrode is centered at the top by the fused quartz collar (4) which is made with a sliding fit so that the inner electrode can be easily removed for cleaning. The temperature is indicated by a thermometer placed in the tube in the top of the inner electrode. The fused quartz insulation was shown to have negligible surface leakage, volume conductivity and dielectric loss.

Before a measurement, the oil to be tested was placed in the cell and carefully evacuated. Then the fused quartz collar was placed in position effectively sealing the oil against the absorption of moisture from the atmosphere. The temperature was controlled by placing the cell in a thermostatically controlled heater.

However, to make certain that absorbed moisture or absorbed gases were not responsible for the observed dielectric loss, the vacuum cell shown in Fig.

2 was prepared. The electrodes were concentric nickel cylinders, 10 cm high and spaced about 2 mm apart. The outer cylinder (1) was supported by two wires sealed into the bottom of the Pyrex cell, one of which acted as the ground lead (2). The inner cylinder (3) was supported only by a stiff wire (4) which was sealed into the top of the cell and served as the other lead. The Pyrex tube (5) supporting the inner cylinder was sealed to the top of the cell wall (6) to form an annular expansion chamber for the oil and also to provide a very long glass path between the two electrodes. A small tube (7) with a closed end was sealed into the bottom of the cell so that the temperature of the oil in the cell could be determined with a small thermocouple.

For filling, two glass tubes extended from the top of the annular chamber. One was sealed to a good vacuum system. The other led through a stop-cock to a reservoir of oil at atmospheric pressure. The oil was heated to about 125°C and allowed to bubble very slowly through the stop-cock thereby liberating all gases. When the cell was filled to a level near the top of the expansion chamber and all bubbling had ceased, both tubes were sealed off leaving completely degasified oil in the cell ready for the electrical measurements.

Tests on this cell before and after filling showed the following:

(a) The dielectric loss in the oil showed the same characteristics as those observed with the quartz insulated cell. (b) The errors of measurement caused by leakage over the surface at low frequencies and by dielectric loss in the Pyrex at high frequencies were greater than for the quartz insulated cell. (c) The actual measurements with the vacuum cell were less accurate because the cell constant was much smaller than for the quartz insulated cell. (d) The errors could have been eliminated by using guard ring electrodes but for commercial oils these complications seemed unnecessary.

For these reasons all subsequent measurements were made with the open, quartz insulated cell and only measurements made with this cell are reported.

2. *D. C. Measurements.*—The source of potential was a 350 volt "B" battery and a sensitive galvanometer with an Ayrton shunt was used to measure the current. The galvanometer calibration was checked before and after each run.

3. *Low-Frequency Measurements.*—A variable frequency vacuum tube oscillator[2] having a range from 200 to 10,000 cycles per second was used to supply a modified General Radio "power factor bridge." The variable capacitance standard was a General Radio precision instrument. This same standard was used for both low and high frequency measurements.

4. *High-Frequency Measurements.*—These tests were made with equipment permanently installed in a well shielded room built especially for radio frequency measurements. The standard substituation method (Bureau of Standards Circular No. 74) was used throughout. The generating circuit was a vacuum tube oscillator having a frequency range from 4×10^4 to 3×10^6 cycles per second. The power rating was sufficient to prevent any change in either the frequency or the voltage when changes were made in the loosely

[2] Gen. Elec. Rev. P. 521, October, 1929.

coupled measuring circuit. The oscillator gave an approximate sine wave, having less than 5 percent harmonic components.

The measuring circuit is shown in Fig. 3. The generating circuit (1) has been discussed above. Coupling coils (2) having from 1 to 10 turns were used depending upon the frequency desired. The measuring circuit was loosely coupled to the generating circuit by the coil (3). The special high frequency switch (4) was used for connecting either the test cell (5) or the standard capacitance (6) into the measuring circuit. The switch was composed of six mercury cups mounted on fused quartz tubes. Amalgamated copper wires were used for making contact between the desired pairs of cups. The current-indicating device in this circuit was a special vacuum thermocouple whose heater resistance had a constant value of 0.72 ohm over the entire frequency range. This type of couple is designed so as to have a long leakage path between the heater leads. The thermocouple was connected through the radio frequency choke (8) to the sensitive galvanometer (9). The sensitivity of the

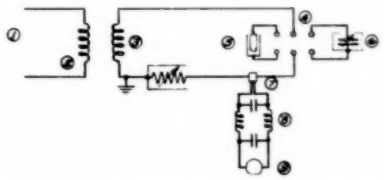


Fig. 3. High frequency measuring circuit.

combination was such that 2×10^{-4} amp. input to the heater of the thermocouple gave approximately 1 mm deflection on the galvanometer scale. The link resistors (10) were made of short straight lengths of non-magnetic, resistance wire sealed in evacuated glass tubes. These were approximately the same length and range from 0.115 to 26.2 ohms. For greater resistances a shielded General Radio decade resistance box, having 0.1 ohm steps, was used.

The procedure for a high frequency measurement differed slightly from that prescribed by A.S.T.M.D. 150-27T, and was as follows:

(a) The supply oscillator was set at the desired frequency and a coupling coil was selected which would resonate with the test cell connected and a short circuiting link at (10). This circuit was then tuned exactly to resonance by varying the supply frequency and the galvanometer deflection recorded. With no further change in the supply oscillator, the standard capacitor was substituted for the test cell and adjusted to give resonance of the measuring circuit. The setting of the standard was then the capacitance of the test cell. If the galvanometer deflection was not the same as it was with the test cell in the circuit, the effective resistance of the circuit must be different. That is, the dielectric loss of the standard capacitance differed from that of the test cell. Since the standard was an air capacitance with good insulation, its dielectric loss was very small and was considered negligible. Link resistors were added in series with the standard capacitance until the deflection was the

same as that recorded for the test cell, thus giving the equivalent series resistance of the test cell. For each point this procedure was repeated several times to make certain of the value obtained and then the exact frequency was determined with a wave meter.

Calculations from A. C. Measurements

The alternating current measurements have been interpreted in terms of the equivalent parallel circuit shown in Fig. 4. C is the equivalent capacitance

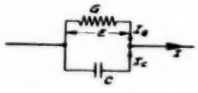


Fig. 4. Equivalent circuit for an imperfect dielectric.

and is considered to have zero loss and zero inductance. G is the equivalent a.c. parallel conductance and is considered to have zero capacitance and zero inductance. This simple equivalent circuit has been used for the following reasons:

(a) The mechanism of dielectric loss in oils is not sufficiently well understood to enable one to represent it exactly in terms of ideal resistances and capacitances. Therefore *a circuit which is assumed to be equivalent rather than one which is theoretically exact, must be used.*

(b) The actual measurements were made with a series connection of a resistance having negligible capacitance and a capacitance having negligible loss. Therefore the interpretation of the results *must be made* in terms of this simple series measuring circuit.

(c). However the parallel circuit is chosen in preference to the series circuit because G represents a coefficient of dielectric loss independent of C. That is, G is proportional to the component of current in the external circuit which is in phase with the applied potential. Therefore it is a measure of the dielectric loss regardless of the mechanism by which that loss may have been produced.

(d). With the coefficient G, the dielectric losses of different materials can be compared without reference to their dielectric constants. It is therefore preferable to the commonly used coefficient of power factor which represents a ratio of dielectric loss to dielectric coefficient and therefore involves two independent characteristics of the material.

(e). Under certain special conditions the equivalent parallel conductance obtained by a.c. measurements is identical with the d.c. conductance so that this method of representing the a.c. measurements is very convenient, in correlating a.c. and d.c. tests.

To obtain the relations between equivalent series and parallel circuits let:

R = the known equivalent series resistance of the test cell
C_s = the known equivalent series capacitance of the test cell
G = the desired equivalent parallel conductance of the test cell
C = the desired equivalent parallel capitance of the test cell
$w = 6.28$ (frequency in cycles per second of the applied potential).

The equivalence between the series and parallel circuits is expressed by the complex relation

$$G + iwC = (R - i/wC_s)^{-1} \tag{3}$$

from which are obtained the two real equations:

$$G = \frac{R}{R^2 + (1/wC_s)^2} \tag{4}$$

and

$$wC = \frac{(1/wC_s)}{R^2 + (1/wC_s)^2}. \tag{5}$$

For good dielectrics the loss component of current is small compared to the capacitance component so that it may be assumed that,

$$R^2 <<< (1/wC_s)^2. \tag{6}$$

With this assumption Eqs. (4) and (5) become:

$$G = Rw^2C_s^2 \tag{4a}$$

and

$$C = C_s \tag{5a}$$

The apparent power factor of a dielectric is generally used as a measure of its quality and may be calculated from either the equivalent series or equivalent parallel circuit. The definition of power factor is:

$$\text{power factor} = \frac{\text{real power}}{\text{apparent power}}. \tag{7}$$

For the series circuit

$$P.F. = \frac{I^2R}{I^2(R^2 + (1/wC_s)^2)^{1/2}} \tag{8}$$

and if $R^2 <<< (1/wC_s)^2$ this reduces to,

$$P.F. = RwC_s. \tag{8a}$$

For the parallel circuit,

$$P.F. = \frac{E^2G}{E^2(G^2 + (wC)^2)^{1/2}} \tag{9}$$

or again if $G^2 <<< (wC)^2$ Eq. (9) reduces to

$$P.F. = G/wC. \tag{9a}$$

Since both low and high frequency measurements were made in terms of an equivalent series circuit, Eqs. (4) and (8) were used to obtain the equivalent parallel conductance and the equivalent power factor of the test samples.

Discussion of Experimental Results

The results of previous tests led to a study of a single oil through a wide range of frequency and temperature. Properties of the oil on which these measurements were made are given in Table I.

Table I. *Physical data for the oil studied.*

(1)	Flash point	280°C
(2)	Fire point	320°C
(3)	Acid value	0.035 milligram of KOH per gram
(4)	Dielectric strength at 30°C	37 kilovolts for 0.1 inch gap
	Dielectric strength at 100°C	29 kilovolts for 0.1 inch gap
(5)	Specific gravity at 30°C	0.9085
	Specific gravity at 100°C	0.8654
(6)	Viscosity at 30°C	11.76 poises
	Viscosity at 100°C	0.27 poises

The equivalent parallel conductance was taken as a measure of the dielectric loss and the results of the entire series of tests are shown in Fig. 5. Inasmuch as no equipment was readily available for measurements at frequencies between 3,000 and 125,000 cycles per second, there is a gap in the data between these frequencies. The curves indicate no sudden change in the characteristics of the oil so that it did not appear necessary to set up special equipment for this frequency range.

The most interesting deductions to be drawn from these data are as follows:

(a). As the temperature is increased all of the curves approach the line representing the d.c. conductance. For example at 150°C the conductance is the same for all frequencies below 125,000 cycles per second since curves (1) through (5) all pass through the point (*a*).

(b). For each frequency there is a temperature below which the total dielectric loss is greater than can be explained by the mechanism of conduction.

These observations may be stated in a slightly different way; namely,

(c). For a given temperature there is a critical frequency such that for all lower frequencies the a.c. loss is independent of the frequency and for all higher frequencies the loss increases with the frequency. Within the first frequency range the mechanism of d.c. conduction and of a.c. loss appear to be the same, and both are probably due to the migration of charged ions or larger particles in the oil.

(d). The higher the temperature, the higher the critical frequency below which the a.c. and d.c. losses are the same.

These data seem to indicate that the total dielectric loss can be separated into two components,—one independent of frequency and due to the same mechanism as d.c. conduction, and the other independent of conduction and varying with both frequency and temperature. In the remainder of this discussion, therefore, the total dielectric loss will be considered to be the algebraic sum of these two components.

$$\text{Total dielectric loss } (P) = \text{d.c. loss } (P_d) + \text{a.c. loss } (P_a) \qquad (10)$$

The name d.c. loss is used as the simplest designation for the component that is independent of frequency and the name a.c. loss is used to mean the component which varies with frequency. They are so separated because it seems that they result from two entirely different effects of the applied potential and are independent of each other as far as their variation with frequency and temperature is concerned.

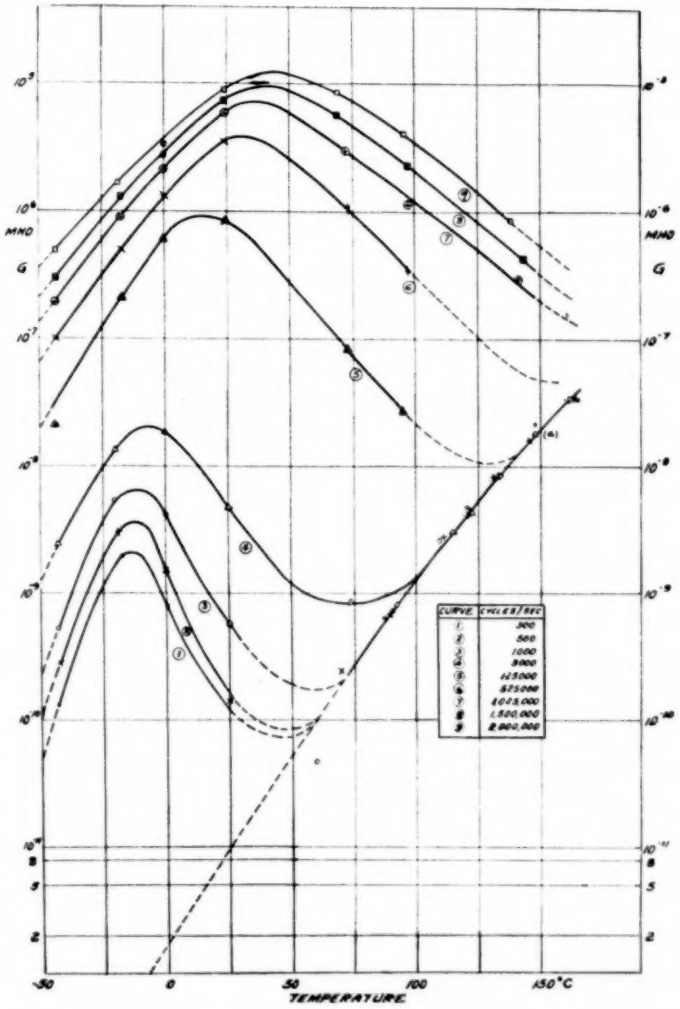


Fig. 5. Total dielectric loss in a heavy cable oil as a function of frequency and temperature. Loss per $cm^3 = (E^2/V)G$ watts/cm^3. E is the potential in volts, G the equivalent parallel conductance in mhos, and V the effective volume of oil in test cell (73.7 cm^3).

These two components are represented by their equivalent conductances as shown in Eq. (10a).

$$P = E^2G = E^2(G_d + G_a) \tag{10a}$$

so that G_a may be obtained as the algebraic difference of G and G_d.

Accordingly the next step in studying these data was to plot curves for $(G-G_d)/f$. As shown in Fig. 6 they give the a.c. loss per cycle as a function of frequency for seven different temperatures. These curves are very interesting since they show that, after the loss due to d.c. conduction has been subtracted, the remainder, when plotted as loss per cycle goes through a maximum as a function of either temperature or frequency. The curves at different temperatures are similar. The higher the temperature (or the lower the viscosity), the higher is the frequency necessary to produce maximum loss.

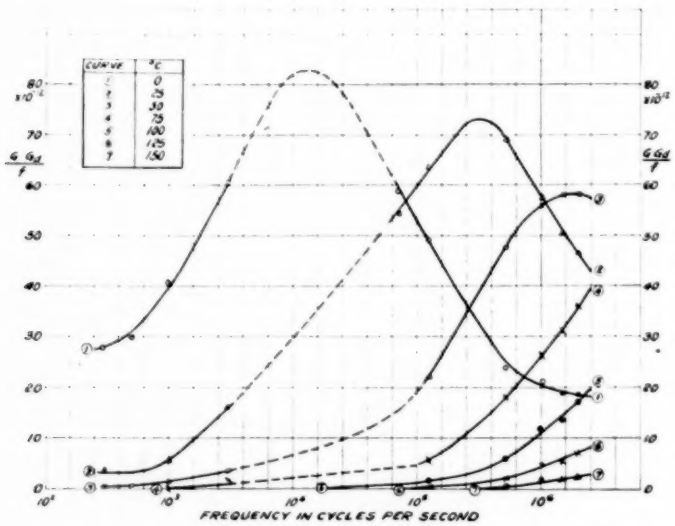


Fig. 6. a.c. loss in a heavy cable oil as a function of frequency for different temperatures. Loss per cycle per cm^3 $=(E^2/fV)(G-G_d)$ joules/cycle/cm^3. E is the potential in volts, G is the equivalent parallel conductance in mhos, G_d is the d.c. conductance in mhos, f is the frequency in cycles per second and V is the effective volume of oil in test cell (73.7 cm^3).

Another and perhaps more usual way of measuring the dielectric loss per cycle per unit volume is to plot the power factor as shown in Fig. 7. From the equivalent parallel circuit the total dielectric loss is given by,

$$P = E^2G \text{ watts} \tag{11}$$

and loss per cycle per unit volume is

$$E^2G/fV \text{ watts per cycle per cm}^3. \tag{12}$$

For low loss dielectrics (power factor less than 10%) we have from Eq. (9a)

$$P.F. = G/2\pi fC$$

from which $G/f=2\pi c$ (P.F.), which when substituted in Eq. (12) gives,

$$\text{loss per cycle per cm.}^3 = (2\pi CE^2/V)(P.F.). \tag{13}$$

This shows that power factor is a coefficient proportional to the dielectric loss per cycle per unit volume, if the capacitance can be assumed constant.

Except for scale, the only difference between corresponding curves in Figs. 6 and 7 is that in the latter the ordinates are proportional to the total loss per cycle while in the former they are measures of the "a.c. loss" only.

From these curves we have an explanation of the *V* curves of power factor as a function of frequency. Consider first curve (7) corresponding to 150°C. Fig. 5 shows the total loss in watts to be independent of frequency below 125,000 cycles per second at this temperature. Therefore in computing power factor, the loss per cycle becomes greater as the cycles per second are de-

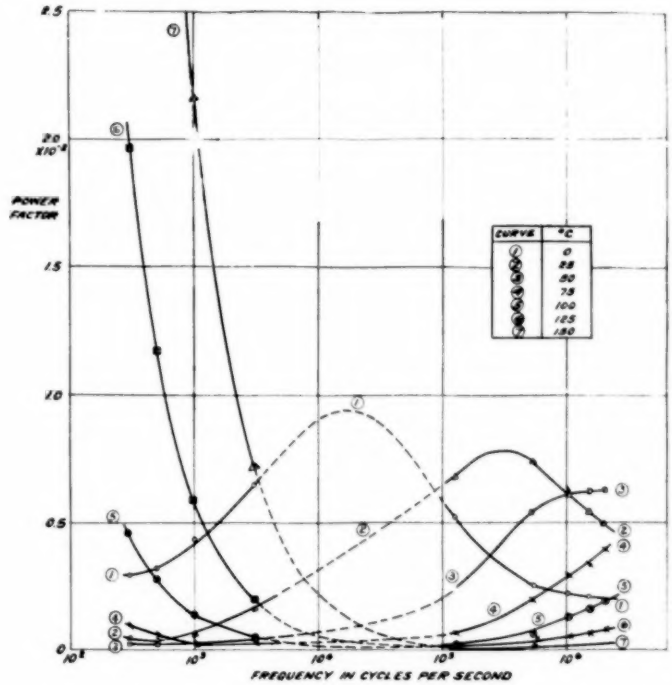


Fig. 7. Total dielectric loss in a heavy cable oil as a function of frequency for different temperatures. Loss per cycle per $cm^3 = (2\pi CE^2/V)$(P.F.) joules/cycle/cm^3. E is the potential in volts, C is the capacitance in farads, and V is the effective volume of oil in test cell (73.7 cm^3).

creased. In other words, as the frequency is decreased, the loss component of current remains constant but the capacitance component decreases with the frequency so that the power factor increases approaching unity as a limit.

Now consider curve (1) corresponding to 0°C. Fig. 5 shows that the d.c. loss is negligible compared to the measured loss and Fig. 6 shows that this a.c. loss per cycle goes through a maximum as a function of the frequency. For intermediate temperatures, the curve may be a combination of these two distinct types. Thus curves (4), (5) and (6) show the descending portions of the d.c. characteristic at low frequencies and the ascending portions of the a.c. characteristic at high frequencies.

To represent more clearly the data shown in Fig. 7 as functions of both temperature and frequency, the curves were cut out of stiff card board and

placed in a frame at equal intervals to represent a three dimensional graph as shown in Fig. 8.

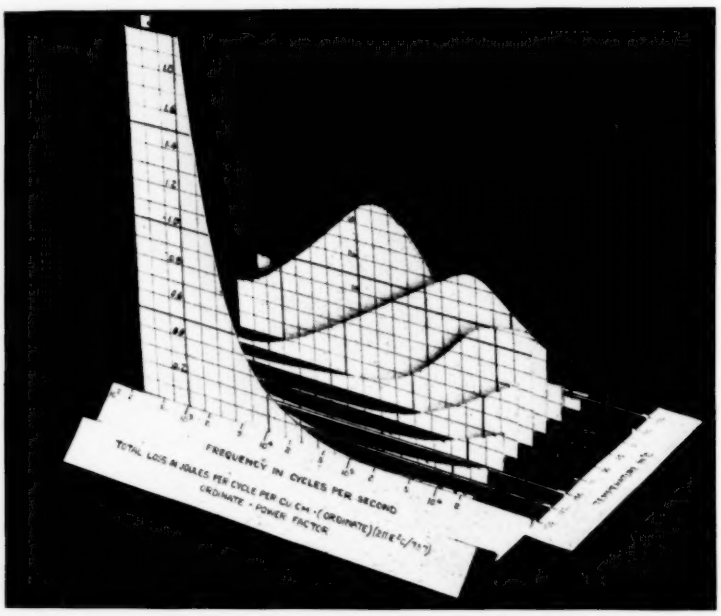


Fig. 8. Variation with frequency and temperature of dielectric loss in heavy cable oil. Composite curve chart.

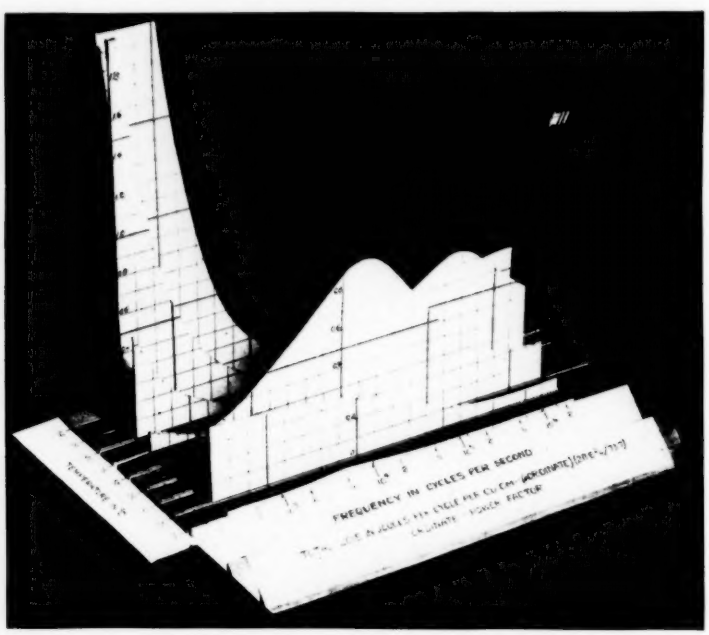


Fig. 9. Variation with frequency and temperature of dielectric loss in heavy cable oil. Composite curve chart.

In Fig. 9 the direction of increasing temperature has been reversed to show the curves that are hidden in Fig. 8. These data show the danger in drawing conclusions as to the character of a material from measurements taken only for narrow ranges of experimental conditions. It is possible to obtain for certain limited areas of this three-dimensional graph either increasing or decreasing power factor as a function of either frequency or temperature. Similar studies over wide ranges of frequency and temperature may explain apparent discrepancies between the results of different experimenters working in different limited ranges of measurement.

Data somewhat similar to these are shown by Emanueli[3] for an oil containing 35 percent rosin. An analysis of these data shows that he did not carry his test to high enough frequencies to obtain maxima in the curves for (G/f) *vs.* (f) similar to those shown in Fig. 6.

Debye's Theory of Polar Molecules

We shall not reproduce the theory as developed by Debye[4] although the attendant assumptions will be indicated in the discussion. As a result of the solution of a differential equation of motion of a polar particle in a viscous medium, Debye arrives at the following relation for the dielectric coefficient* of the medium,

$$\epsilon = \frac{\left(\frac{\epsilon_0}{\epsilon_0 + 2}\right) + i\omega\tau\left(\frac{\epsilon_\infty}{\epsilon_\infty + 2}\right)}{\left(\frac{1}{\epsilon_0 + 2}\right) + i\omega\tau\left(\frac{1}{\epsilon_0 + 2}\right)} \tag{14}$$

where-

ϵ_0 = dielectric coefficient at zero frequency

ϵ_∞ = dielectric coefficient at infinite frequency

or ϵ_∞ = (refractive index)^2

τ = relaxation time

ω = 6.283 (cycles per second).

By expanding Eq. (14), this relation can also be written in the form,

$$\epsilon = \epsilon' - i\epsilon'' \tag{14a}$$

where

$$\epsilon' = \frac{\epsilon_0(\epsilon_\infty + 2)^2 + \omega^2\tau^2\epsilon_\infty(\epsilon_0 + 2)^2}{(\epsilon_\infty + 2)^2 + \omega^2\tau^2(\epsilon_0 + 2)^2} \tag{15}$$

and

[3] L. Emanueli, High Voltage Cables, P. 38, (John Wiley & Sons, 1930).

[4] P. Debye, "Polar Molecules," The Chemical Catalog Co., 1929.

* This is usually called "dialectric constant," but as pointed out by Addenbrook in Nature **126**, 808 (1930), the quantity varies considerably with different experimental parameters and therefore might better be called "dielectric coefficient."

$$\epsilon'' = \frac{\omega\tau(\epsilon_0 - \epsilon_\infty)(\epsilon_\infty + 2)(\epsilon_0 + 2)}{(\epsilon_\infty + 2)^2 + \omega^2\tau^2(\epsilon_0 + 2)^2}. \tag{16}$$

At this point we shall depart from the method of Debye, who, because of similarity with optical phenomena interprets the dielectric coefficient in terms of the relation,

$$\epsilon = r^2(1 - ik)^2 \tag{17}$$

where r and k are the indices of refraction and absorption. Our experience indicates that the data can be analyzed without the use of the optical index of absorption.

In Eq. (14a), ϵ' is the true dielectric coefficient in the ordinary usage of the term, since it is a measure of the current in the external circuit which leads an applied sinusoidal potential by 90°. ϵ'' being at right angles to ϵ' is really a measure of the current which is in phase with the applied potential and therefore proportional to the dielectric loss. The relation between ϵ'' and G in Eq. (3) may be shown as follows:

In the equivalent parallel circuit

$$Y = (\text{admittance}) = (\text{impedance})^{-1} = G - iw\epsilon' C_v \tag{18}$$

where

$$\epsilon' = C/C_v \tag{19}$$

according to the definition that the dielectric coefficient is the ratio of the capacitance with a given material as a dielectric, to the capacitance of the same system with vacuum as a dielectric.

Using Debye's generalized dielectric coefficient from Eq. (14a) to account for both the in-phase and out-of-phase components of the current we have,

$$Y = 0 - iwC_v(\epsilon' - i\epsilon'') \tag{20}$$

which when expanded gives,

$$Y = w\epsilon'' C_v - iw\epsilon' C_v. \tag{21}$$

By comparing Eq. (18) and (21), we have a relation between our equivalent parallel conductance G and Debye's imaginary component ϵ'' of the generalized dielectric coefficient, namely

$$G = w\epsilon'' C_v. \tag{22}$$

For a given test cell, C_v is a constant so that ϵ'' is proportional to G/f. Therefore the curves in Fig. 6 are directly proportional to Debye's ϵ'', for conditions under which the d.c. conductance is negligible.

The next logical step is therefore to set the first derivative with respect to w of Eq. (16) equal to zero, and obtain a relation for the frequency at which

the loss is a maximum. The result of this operation is that ϵ'' should be a maximum when,

$$w\tau = (\epsilon_\infty + 2)/(\epsilon_0 + 1). \tag{23}$$

Now, if this value be substituted back in Eq. (16) we have,

$$\epsilon_m' = \tfrac{1}{2}(\epsilon_0 + \epsilon_\infty) \tag{24}$$

and

$$\epsilon_m'' = \tfrac{1}{2}(\epsilon_0 - \epsilon_\infty) \tag{25}$$

ϵ_0 and ϵ_∞ are independent of frequency and change with temperature, only as the density changes. Therefore Eq. (23) indicates that *the frequency at which the maximum loss occurs will vary inversely with the relaxation time of the polar molecules.*

Debye develops the following relation for the relaxation time

$$\tau = 4\pi\eta a^3/kT \tag{26}$$

where

η = the coefficient of viscosity in poises
a = the effective radius of the polar molecule in cm
k = Boltzmann's constant = 1.37×10^{-16}
T = absolute temperature.

Eq. (25) indicates that except for changes with temperature due to changes in density, *the maximum value of the loss per cycle should be independent of temperature or frequency.*

The assumptions made by Debye in developing this theory may be stated briefly as follows:

(a). The solution of polar molecules in a non-polar solvent is sufficiently dilute so that the interaction between neighboring polar molecules is negligible.

(b). The laws of an ideal gas may be applied and use made of Boltzmann's constant and Avogadro's number.

(c). Viscosity coefficients, as ordinarily measured, and Stoke's law for falling spheres in a viscous medium may be applied to forces between polar and non-polar molecules.

Of these assumptions the third is probably the one which is most open to criticism in applying this theory to a viscous mineral oil.

There is more evidence that insulating oils contain charged particles than that they contain polar molecules. Therefore it may be possible that mathematical relations, which would also explain experimental observations, could be developed for the motion of charged particles in a viscous medium.

In a recent discussion of Debye's theory, Whitehead[5] sets up a relation for

[5] S. Whitehead. Phil. Mag. **9**, 865 (1930).

power factor in terms of the physical coefficients of the material instead of in terms of the limiting values of ϵ as suggested by Debye. Whitehead then differentiates this expression with respect to w to determine the conditions for maximum power factor.

The development we have given above seems much preferable to that suggested by Whitehead for the following reasons:

(a). The limiting values of the dielectric coefficient ϵ_0 and ϵ_∞ can be measured more easily and more accurately than the electric moment and the molecular viscosity, which are required to evaluate Whitehead's relations.

(b). The study of power factor relations is inherently more complicated than the study of the loss coefficient alone, because the former involves a ratio between two quantities which vary as different functions of temperature and frequency.

(c). Not only is it easier to measure separately the capacitance and the loss coefficients, but such a study will lead to a clearer understanding of both, than is possible from a determination of power factor, which measures only their ratio.

Quantitative Check of Debye's Theory

To apply the above theory to our experimental data, the following quantities were determined for 25°C:

$\epsilon_0 = 2.30$

$\epsilon_\infty = (\text{refractive index})^2 = (1.5077)^2 = 2.27$

$C_v = 65.1 \times 10^{-12}$ farads

and f_m = frequency at which the maximum loss per cycle occurs = 316,000 cycles per second.

Using these particular values and Eqs. (16) and (22), a curve of (G/f) against frequency can be calculated and plotted as shown in Fig. 10. The difference between the calculated and observed maximum ordinate can be easily explained as an experimental error. According to Eq. (25) the maximum ordinate is proportional to the difference between ϵ_0 and ϵ_∞. This difference is only 1.3 percent of the measured values, so that a 1 percent error in either coefficient would cause of 75 percent error in their difference. The index of refraction should be accurate to 0.1 percent but ϵ_0 might easily be in error by 0.5 percent, since the measurement was made before the need for such extreme accuracy was recognized. Thus the *maximum ordinate may be considered to check the theory within the limits of experimental accuracy.*

Eq. (16) shows that $(\epsilon_0 - \epsilon_\infty)$ enters as a multiplying factor for all frequencies, so that even though ϵ_0 were corrected to give an agreement between the maxima of the two curves, their shapes would be entirely different. This indicates that, *while the order of magnitude is correct, the theory in this simple form is not sufficient to predict quantitatively the observed results.* An obvious and possible explanation of the difference in the shapes of the experimental and

theoretical curves is that the theory postulates particles of only one size. If there are any polar particles in the oil they are probably of many different sizes, so that a much broader frequency responce is obtained than would be given by the presence of particles of only one size.

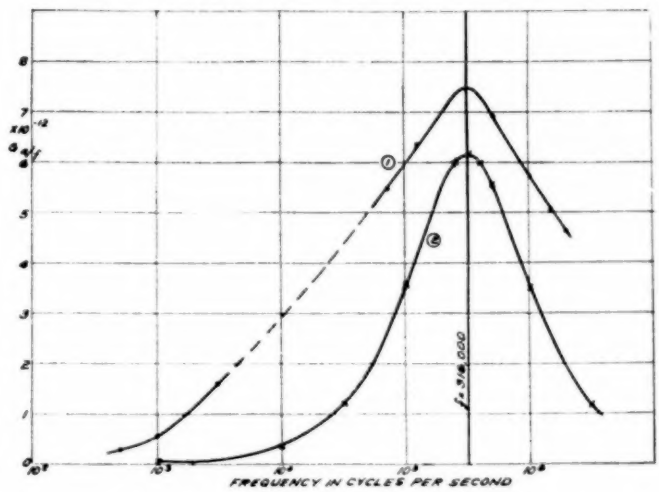


Fig. 10. a.c. loss per cycle for a heavy cable oil at 25°C. Curve 1 from observed data, curve 2 calculated from Debye's theory of polar molecules.

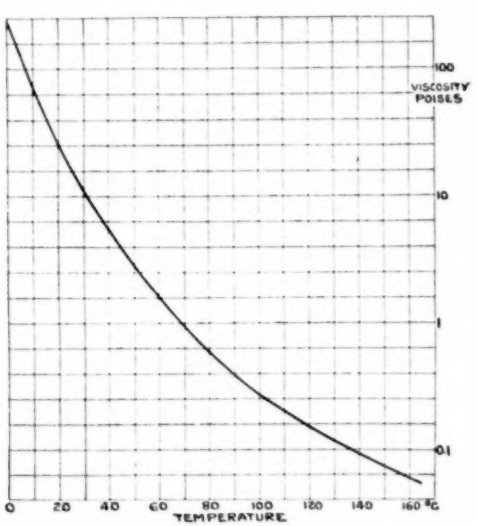


Fig. 11. Viscosity characteristic of a viscous cable oil.

Another indication of the validity of the theory may be obtained by determining the effective radius of the polar particles from Eq. (26). This can be done by reading from the curves in Fig. 6, the frequency at which each isothermal curve is maximum. Then τ can be determined for each tempera-

ture from Eq. (23), so that it is possible to solve for (a) in Eq. (26). The results of such a calculation are shown in Table II.

TABLE II. *Calculation of size of polar molecule.*

T °C	ϵ_∞	ϵ_0	$\omega\tau$	f cyc/sec $\times 10^5$	τ $\times 10^{-7}$	η Poise	a cm $\times 10^{-8}$
0	2.31	2.34	.993	16.	98.7	230	5.04
25	2.27	2.30	.993	316.	5.0	17	4.58
50	2.23	2.26	.993	2000.	0.79	2.9	4.59

As the temperature of the oil is increased the viscosity decreases rapidly according to Fig. 11. Therefore the relaxation time decreases very rapidly with increased temperature resulting in a corresponding large increase in the frequency necessary to cause maximum loss as shown in Fig. 6.

Here again we have a qualitative check of the theory in that three determinations for the calculated size of particles agree fairly well and the value obtained is of the right order of magnitude.

The author is pleased to express his indebtedness to Mr. S. I. Reynolds of the General Electric Company for his careful work in making the high frequency measurements reported in this paper.

LETTERS TO THE EDITOR

Prompt publication of brief reports of important discoveries in physics may be secured by addressing them to this department. Closing dates for this department are, for the first issue of the month, the twenty-eighth of the preceding month; for the second issue, the thirteenth of the month. The Board of Editors does not hold itself responsible for the opinions expressed by the correspondents.

Wave-length Measurement of Gamma-Rays from Radium and its Products

In my paper on the γ-ray spectrum of radium and its products (Phys. Rev. [2] **36,** 460 (1930)) it was pointed out that the peaks appearing on the intensity curve and interpreted as γ-ray lines were sharp, and were apparently resolved by the spectrometer when the glancing angles of reflection from calcite differed as little as 20 seconds of arc, although the geometry of the arrangement did not account for such high resolving power.

Professor Niels Bohr in private correspondence with Professor Kovarik has emphasized the importance of this question concerning resolution in my experiments, and a further study of the matter has shown that the discrepancy between the resolving power as estimated from the experimental curves and that computed from the dimensions of the apparatus is greater than can be accounted for by any reasonable hypothesis regarding accidental inclination of the slit faces. He also points out that besides this there is a further difficulty in connection with the apparently great relative intensity of the very short wave-length lines or bands. Theories of scattering predict much lower intensity for scattered radiation of such high frequency. The reality of the reported results thus assumes considerable theoretical importance and needs more experimental justification.

It is impossible to give, at present, any other interpretation of the experimental results than that first offered. It is my intention, therefore, to reinvestigate the problem with improved apparatus. Meanwhile the question regarding the existence or non-existence of new lines of strong intensity in the γ-ray spectrum of radium and its products must be left open.

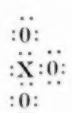
LUVILLE T. STEADMAN
University of Rochester,
Rochester, New York,
January 21, 1931.

Arrangements of Atoms in Crystals

In the January 1st number of the Physical Review (**37,** 105 (1931)) is an abstract of a paper by Zachariasen in which the author reports the results of crystal structure investigations of $KBrO_3$, KCl_3, $NaClO_3$ and Na_2SO_3. He finds, in agreement with the earlier work on $NaClO_3$ and $NaBrO_3$ (Kolkmeijer, Bijvoet and Karssen, Verslag akad. Wetenschappen Amsterdam **23,** 644 (1920); Dickinson and Goodhue, J. Am. Chem. Soc. **43,** 2045 (1921)) that the XO_3 groups in these crystals can be described as "tetrahedral groups with one tetrahedral corner removed," and notes that this is a similar arrangement to that around As or Sb in As_2O_3 crystals (Bozorth, J. Am. Chem. Soc. **45,** 1621 (1923)). The statement is then made that in each case "the cation has got only 2 electrons in the outer shell," the non-coplanar arrangement being explained "as due to deformation in the outer shell of the cation, where the charge distribution is very diffuse."

It seems more likely to the writer that these are merely cases of shared electron pairs, as postulated by G. N. Lewis ("Valence and the Structure of Atoms and Molecules," Chem. Cat. Co., New York, 1923). The total number of valence electrons in each of these ions is 26, and if Lewis is correct, that there is a tendency toward the completion of valence shells containing eight electrons (four pairs tetrahedrally oriented) around the kernel of every electronegative atom, the distribution in space of the atoms must be similar to that observed,

the electrons being shared as indicated by the formula



In the case of the oxides of arsenic and antimony, there are five electrons per As or Sb and six per O. To complete a four-pair tetrahedral valence shell around each atom requires that each As or Sb shares 3 electron pairs, at tetrahedron corners, with 3 oxygen atoms and each oxygen shares 2 pairs, at tetrahedron corners, with two As or Sb atoms,—precisely the arrangement determined from x-ray data.

It is plain that one can not only predict from this theory the number of electron pairs (per molecule or crystal unit) shared between electronegative atoms, but one can also predict that if an electronegative atom is adjacent to 2, 3, or 4 others, the arrangement will be that of 2, 3, or 4 corners of a (not necessarily regular) tetrahedron around its center.

Such predictions can be tested very readily by the results of x-ray analysis and in general they are found to be in agreement with experiment. Thus in iodine the negative atoms are in pairs; in crystals of Se and Te, each atom is adjacent to two others in a spiral chain; in P, As, Sb and Bi the atoms are in puckered layers, each adjacent to three others at three corners of a tetrahedron, while in the diamond, Si, Ge and gray Sn each atom in tetrahedrally surrounded by four others. Among compounds, several have been mentioned already; many others might be given.

As Lewis readily admits, there are exceptions to this tendency. Examples he gives are the molecules SF_6 and PCl_5 in which the central P and S atoms probably have 5 and 6 valence pairs, respectively. Other examples are afforded by such compounds as $CsICl_2$ and CsI_3, in which the three halogen atoms form a colinear group. The number of valence electrons (counting 7 per halogen and 1 per Cs) in each X_3 ion is 22. The most reasonable distribution of these would seem to be one in which the central atom has 5 pairs and each of the others four.

In $CaCO_3$ and $NaNO_3$ both crystallographic and x-ray data indicate a 3-fold axis of symmetry through each C and N center and two-fold axes of symmetry through each C-O and N-O centerline. If the oxygen tetrahedra are oriented in agreement with this symmetry, each C or N kernel is surrounded by six pairs, joining it by double bonds to the neighboring oxygens.

The four pair valence shell is apparently stable if the valence shell is not made too large (as by the pull of surrounding electron atoms) in which case more pairs can be accommodated. The smaller the kernel charge—in general, the more electropositive the atom,—the more pairs can be accommodated in the valence shell but the less tightly each is held. Although in quartz (SiO_2), HgI_2, ZnS, AgI and many other compounds relatively electropositive atoms are surrounded by four electronegative atoms at tetrahedron corners, suggesting electron sharing with tetrahedral valence shells around *all* the atomic kernels, in many others the electropositive atoms are surrounded by six or eight negative atoms. In some cases, (e.g. NaCl) the valence shells of the latter cannot be oriented so as to place the valence pairs on the centerlines between adjacent atoms; evidently in such polar crystals other considerations, such as the relative sizes of the atoms (or ions) are of the greatest importance in determining the type of arrangement. (Cf. Pauling, J. Am. Chem. Soc. **51,** 1010 (1929); Huggins, J. Phys. Chem., in print.)

It should perhaps be pointed out that the point of view taken here is quite in agreement with recent developments in wave mechanics theory. (Cf. Bartlett, Phys. Rev. **36,** 1096 (1930) and papers by Bartlett and by Slater at the Cleveland Meeting of the American Physical Society.) The pairing of valence electrons, the sharing of such pairs between two atoms, and preferred orientations of electron orbits, once bones of contention between physicists and chemists, can now be agreed to by both.

MAURICE L. HUGGINS

Stanford University,
Palo Alto, California,
January 27, 1931.

Energies and Wave-Functios of the State (1s) (2s) ^1S in Helium-like Atoms

Eckart, in the Physical Review, September 1, 1930 (pp. 878 *et seq.*) pointed out that his modification of the Ritz method there presented fails when applied to a state other than the lowest of a given series, e.g. $(1s)(2s)\,^1S$ of helium-like atoms, and suggested that a pro-

cedure might be worked out for applying the method to this case. This has been done by the author, using a comparison function designed to be orthogonal to the wave-function of the ground state.

The following comparison function is orthogonal to the exact wave-function ψ_1 of the ground state: $K(\phi_2-\gamma_1\psi_1)$, where ϕ_2 $=[u(\alpha 1)v(\beta 2)+u(\alpha 2)v(\beta 1)]/[2(1+b^2)]^{1/2}$, $b^2=(2x)^3(x-1)^2/(x+\frac{1}{2})^8$, $x=\alpha/\beta$ (Eckart, Phys. Rev. **36,** 886), ψ_1 = exact wave-function of ground state, $\gamma_1=\int\phi_2\psi_1 d\tau$, $K=[1-\gamma_1^2]^{1/2}$. Actually the use of a very accurate wave-function for ψ_1 (such as that of Hylleraas), was found to introduce too great complexities into the maximization. The function ϕ_1 $=[u(\epsilon 1)u(\eta 2)+u(\eta 1)u(\epsilon 2)]/[2(1+c^2)]^{1/2}$, where $c^2=64(\epsilon\eta)^3/(\epsilon+\eta)^6$, was used for ψ_1, (due to Eckart, Phys. Rev. **36,** 883). The validity of this approximation can be judged from the fact that a 10% change in γ_1^2 was found to produce only a 1% change in the calculated ionization potential. The parameters ϵ and η correspond to Eckart's α and β for the state $(1s)^2$.

This comparison function gave the results summarized in the following table (α_0 and β_0 are the adjusted values of the parameters, $R_\infty h$ = unit of energy, W = energy, V_i = ionization potential):

	Z	α_0	β_0	W (calc.)	W (obs.)	V_i (calc.)	V_i (obs.)
He I	2	2.00	1.17	4.289	4.292	0.289	0.292
Li II	3	2.98	2.19	10.073	10.082	1.073	1.082
Be III	4	3.97	3.18	18.361	—	2.361	—
B IV	5	4.97	4.19	29.146	—	4.146	—

One notices that α_0 is approximately equal to Z, $(Z-\alpha_0\backsim 0.02)$; that $Z-\beta_0$ is essentially constant and $\backsim 0.82$; and that W(calc.) $=(5/4)Z^2+aZ+b$, where $a=-0.464$, $b=0.216$.

Hylleraas (Zeits. f. Physik **65,** Heften 11 and 12, Nov. 14, 1930) has recently performed a calculation of this term for the special case of He I; his method, which results in a much more complicated wave-function, yields the value 0.290.

JOHN P. VINTI

Massachusetts Institute of Technology,
January 29, 1931.

A Theory of Collision Processes Involving No Radiation of Energy

The writers have developed a generalization of the Born collision method for dealing with collision processes. In the usual Born method the zero-order wave function for the colliding particle is a plane wave, undistorted by the presence of the stationary particle; which is so poor an approximation that the series for the cross section for many processes diverges; and in every case the first term is a bad approximation for small relative velocities. The writers use as a zero-order wave function one already distorted by an approximate mutual interaction field. The interaction energies effecting the transition have been expanded in a series which converges well for energies less than about 100 electron-volts. The cross sections for the various processes can be then computed and are valid for all except very large relative kinetic energies.

These cross sections, as a function of the size of the particles, of the nature of the transition caused by the impact, of the mutual kinetic energy, and of the energy transferred from kinetic to energy of excitation, check quantitatively with such widely different experimental data as: Bleakney's[1] curves for ionization of Hg; Zemansky's[2] curves for transfer of excitation; Hanle's[3] curves for excitation of various atoms; and Latyscheff and Leipunsky's[4] curves for collisions of the second kind.

PHILIP M. MORSE
E. C. G. STUECKELBERG

Institute for Theoretical Physics,
The University, Munich,
January 29, 1931.

[1] Bleakney, Phys. Rev. **35,** 139 (1930).
[2] Zemansky, Phys. Rev. **36,** 933 (1930).
[3] Hanle, Zeits. f. Physik **54,** 848 (1929).
[4] Latyscheff and Leipunsky, Zeits. f. Physik **65,** 111 (1930).

BOOK REVIEWS

Ergebnisse der Exakten Naturwissenschaften. Vol. VIII. E. BRÜCHE, Freie Elektronen als Sonden des Baues der Molekeln. Springer, Berlin, 1929.

This article deals primarily with experiments on passage of very slow electrons through gases. Stimulated by the observations of Ramsauer, a number of papers in this field have appeared within the last ten years. The present article gives a valuable critical survey of this work including a few new results. In his early paragraphs the author takes great pains to explain the significance of the "effective cross-section" in different types of apparatus. This is essential and well done. Later on almost equally elaborate discussions are given concerning points of minor significance. However, one may well overlook this lack of balance and rejoice to have a clear and systematic presentation of the experimental results including a classification of the "WQ" (Wirkungsquerschnitt) curves into four distinct types. The interpretation of these results can hardly be satisfactory without a consideration of energy losses of electrons in collisions, a field that is outside the scope of this article.

H. D. SMYTH

The Wave Mechanics of Free Electrons. G. P. THOMSON. Pp. 161, figs. 53. McGraw-Hill, 1930.

This book contains the subject matter of lectures delivered by the author as George Fisher Baker Non-Resident Lecturer in Cornell University. As the title implies, the book deals with that part of the subject which concerns electrons not forming part of an atom. It is primarily concerned with an account of experimental work, but also contains a treatment of the theory which is immediately applicable.

After an introductory lecture, the first two chapters treat the General Theory of Waves and de Broglie's Wave Mechanics, respectively. The following 8 chapters include a brief account of the Theory of Wave Diffraction by Crystals, a discussion of various diffraction experiments confirming de Broglie's relation for the wave-length of the electron; the effect on electron diffraction of an inner potential and the resulting refractive index; a discussion of the author's own work on the determination of the atom form factor from intensity measurements, and a theoretical interpretation of certain aspects of these experiments; an outline of Sir J. J. Thomson's physical theory of electron waves; theoretical considerations of the possibility of electron polarization with a list of the various experimental attempts to detect a possible polarization effect; and finally the application of electron diffraction to the study of surface films.

The following errors are noted. Under the discussion of the reviewer's results on pages 101, 102, it is stated that the inner potential Φ was calculated "by subtracting the actual voltage of the electrons from the voltage V given by $V=150/\lambda^2$, where λ is the wave-length in Angstrom units which would give a spot in the observed position, ignoring refraction. This process is equivalent to ignoring the bending of the waves on emerging from the crystal." This is incorrect since the wave-length λ as used in the equation referred to is not that which would give a spot in the observed position, ignoring refraction, but is the theoretical wave-length, determined from the geometry of the crystal for unit refractive index, with which an experimental beam is associated. The colatitude angles for the theoretical and experimental beams are not the same so that the bending of the waves on emerging from the crystal has not been ignored.

On page 102 M. Davis is incorrectly referred to as Miss.

To my knowledge this is the first collection into book form of the experimental investigations in this new field, and will be a valuable reference to the status of the work at the time the book was written (Jan. 31, 1930), although several important contributions have since been made. It is particularly fitting to have an account by a pioneer worker who has made many notable contributions in this field.

H. E. FARNSWORTH

Textbook of Practical Physical Chemistry. K. FAJANS AND J. WÜST. Pp. 233+xiv, figs. 74. E. P. Dutton, New York, 1930. Price $4.95.

The experiments outlined in this book cover a much wider range of subjects than is customary in manuals of physical chemistry. In addition to the material commonly presented, there are chapters on Adsorption from Solutions, Coagulation of a Sol by Electrolytes, Transformation of Radio-Elements, Quantitative Spectrophotometry, Electrochemical Preparations, and the Lead Accumulator. The outlines of the more common experiments follow the classical methods quite closely.

Each chapter is preceded by an unusually complete and worthwhile discussion of the related theory. Numerous references are given to the better known textbooks of theoretical physical chemistry. The description of the experimental procedure is apparently planned to render the student practically independent of the help of a laboratory instructor. The apparatus and experiments are described with meticulous detail, and in several cases this description is followed by a discussion of the probable difficulties and ways of avoiding or overcoming them.

The reviewer feels that it is regrettable that the authors decided to present the experiments on solutions, including the chapter on electromotive force, in terms of the older theory. The authors state in the preface "that to introduce the new system into this book would involve too great a departure from the treatment at present given in most of the general textbooks." This statement certainly does not apply to two of the better-known general texts to which many references are made in this book.

The text bears little evidence that it is a translation from the German; the style is throughout clear and readable. Without resorting to small type, the publishers have been successful in economizing space by their arrangement of the print, so that a large amount of material is presented on 230 pages.

ROBERT LIVINGSTON

Band Spectra and Molecular Structure. R. DE L. KRONIG. Pp. x+163, figs. 16. The Macmillan Company, New York, 1930. Price $3.50.

Books on band spectra are appearing, and more are promised. The volume under review is brief and devoted almost exclusively to the theoretical side of the subject. That, however, is as it should be. If each author will confine himself to those aspects of the field with which he is thoroughly conversant, we will get a set of books which, collectively, will be both authoritative and useful. This volume makes a good start in that direction. In spite of its brevity, it covers a multitude of topics, including an entire chapter on "Macroscopic Properties of Molecular Gases" (scattering, dispersion, Kerr and Faraday effects, dielectric constants, etc.). The range of material is indicated by a few sub-titles, chosen almost at random: Stark and Zeeman Effects, Energy Levels of Polyatomic Molecules, Rotational Distortion of Spin Multiplets, Perturbations and Predissociation, Band Spectra and Nuclear Structure. Moreover, the author kindly marks off those sections for which a knowledge of wave mechanics is essential, and even summarizes their contents, so that the "experimental physicist" may omit such sections without losing the continuity of the argument. I am sure this will be appreciated by the great majority of readers. A few more diagrams, however, might well have been used.

It is not surprising, in a theoretical book, to find an occasional mis-statement of experimental fact. The reviewer was, however, really startled to read, on page 97, that Birge and King had discovered the isotopes of oxygen (as well as that of carbon), and that these discoveries had been made by means of the appearance of the alternate lines which are missing or weakened in the spectra of homonuclear molecules. Such errors are perhaps not serious, for the reader, but Giauque and Johnston may well object, from the personal standpoint. Their beautiful articles on the discovery and confirmation of the oxygen isotopes are not even listed in the *very* extensive and valuable bibliography which concludes the volume.

The author states that he has used the new nomenclature recently recommended by band spectroscopists (R. S. Mulliken, Phys. Rev. **36**, 611, 1930), and this is the case, with a few more or less unimportant exceptions. In just one instance, however, the reviewer considers the matter not unimportant. Dr. Kronig uses unprimed and primed symbols for upper and lower levels,

respectively, whereas the National Research Council committee, after considerable correspondence, recommended in 1926 single and double primed symbols, and this recommendation has been almost universally followed since that time.

These criticisms are not to be taken as an adverse judgment on the volume, as a whole. Many persons will welcome a brief, clear and comprehensive account of the recent important theoretical developments in the field of band spectra, and the present volume gives just such information.

RAYMOND T. BIRGE

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY

MINUTES OF THE CLEVELAND MEETING, DECEMBER 30–31, 1930

The Thirty-second Annual Meeting (the 168th regular meeting) of the American Physical Society was held in Cleveland, Ohio at the Case School of Applied Science and Western Reserve University on Tuesday and Wednesday, December 30 and 31, 1930, in affiliation with Section B—Physics— of the American Association for the Advancement of Science. The presiding officers were Professor Henry G. Gale, President of the Society, Dr. W. F. G. Swann, Vice-president, and Professor F. W. Loomis. The average attendance was about 300.

The annual joint session with Section B was held on Wednesday morning. The presiding officer was Professor F. K. Richtmyer, Vice-president of Section B. The program consisted of the address of the Retiring Vice-president of Section B, Professor Charles E. Mendenhall, on the subject, "Recent Developments in Photoelectricity." This address was followed by a Symposium on Acoustics consisting of three invited papers, as follows: "Recent Development in Architectual Acoustics" by Dr. Paul E. Sabine of the Riverbank Laboratories; "Some Physical Characteristics of Speech and Music" by Dr. Harvey Fletcher of the Bell Telephone Laboratories, Inc.; and "Concerning Some of the Problems Encountered in Recording and Reproducing Photographic Sound Records on Moving Picture Film," by Dr. Clarence W. Hewlett of the General Electric Company. The attendance at this session was 350.

On Tuesday evening the Society joined with the Society of Sigma Xi for dinner at the Cleveland Club after which they attended a lecture by Dr. C. E. K. Mees, of the Eastman Kodak Company, given in the auditorium of the John Hay High School.

Annual Business Meeting. The regular annual business meeting of the American Physical Society was held on Tuesday afternoon, December 30, 1930, at 2:00 o'clock in the lecture room of the Case School Physics Laboratory. A canvass of the ballots for officers resulted in elections for the year 1931 as follows:

President:	W. F. G. Swann
Vice-president:	Paul D. Foote
Secretary:	W. L. Severinghaus
Treasurer:	George B. Pegram
Members of the Council, four year term:	W. D. Coolidge
	F. W. Loomis
Members of the Board of the Physical Review, three year term:	A. J. Dempster
	D. M. Dennison
	J. C. Slater

The Secretary reported that during the year there had been 189 elections to membership. The deaths of 11 members have been reported during the year; 36 have resigned and 28 have been dropped. The membership of the Society as of December 29, 1930 is as follows: Members: 1963; Fellows: 516; Honorary Members: 5; Total Membership: 2484.

The Treasurer presented a summary of the financial condition of the Treasury of the Society. The complete audited report has been printed and distributed to all members.

The Managing Editor presented an informal report stating that the journals of the Society were being well received by the membership as well as by physicists in foreign countries. The financial condition was reported to be one that needed careful attention since the continually increasing quantity of publication brought about an increasing financial deficit which had to be met by the generosity of individuals or organizations. The complete audited financial report of the Managing Editor has been printed and distributed to all members.

Revision of By-Laws. On motion it was voted to approve the recommendation from the Council that Article VI of the By-Laws be changed to read:

> "Each fellow or member of the Society who has paid his dues in full shall receive the Physical Review published by the Society and Science Abstracts Section A—Physics."
>
> (Omit paragraph 2 as superfluous.)
>
> Place sentence regarding Science Abstracts—Section B—with footnote concerning Reviews of Modern Physics.

Important Resolutions. On motion the Society voted approval of the following resolutions passed by the Council;

1. That the Council approve the establishment of a Journal of Applied Physics, with the first issue appearing July 1, 1931, and that the editor of the Physical Review be appointed editor of this journal.
2. That the Council authorize the substitution of a subscription for the Reviews of Modern Physics (or a subscription for the proposed Journal of Applied Physics, if and when established) in lieu of a membership subscription for the Physical Review in the case of any member or fellow who so desires.
3. That the Council approve, in principle, the formation of sections in the Society by subjects and also the encouragement of affiliation of local physics clubs.
4. That the Council propose the formation of an Institute of Physics for the purpose of coordinating various societies whose interests are primarily in the field of physics and for the purpose of supporting their publications.

Resolution number 4 was approved with the addition:

> "That the Council consider specifically the possibility of such organization under Section B of the American Association for the Advancement of Science."

Meeting of the Council. At its meeting held on Monday, December 29, 1930, three persons were elected to fellowship, seven persons were transferred from membership to fellowship, and thirty-eight were elected to membership. *Elected to Fellowship:* J. Frenkel, Otto Oldenberg and W. H. Zachariasen. *Transferred from Membership to Fellowship:* Thomas H. Johnson, Julian E. Mack, George F. McEwen, Chester Snow, Thomas Spooner, Harvey E. White and John G. Winans. *Elected to Membership:* John Bardeen, B. Franklin Blair, L. W. Chubb, C. W. Curtis, R. K. Dahlstrom, R. L. Echols, Russell, Fanning, Sherman L. Gerhard, Edith Gideon, Lynn G. Howell, David R. Inglis, H. D. Koenig, J. B. Horner Kuper, W. Wallace Lozier, Charles H. Lutz, Alfred F. Meyer, Parry H. Moon, Lewis M. Mott-Smith, Willard J. Poppy, Charlotte Purdy, Russell W. Raitt, G. H. Rockwood Jr., Paul N. Russell, Frances O. Severinghaus, G. D. Shallenberger, Paul E. Shearin, Klaus J. Sixtus, Louis Statham, Paul Talmey, Josiah Taylor, George S. Thomas, Kenneth, B. Thomson, Louisa E. Townshend, John F. Wagner, Clarence W. Wallace, Charles A. Whitmer, Ralph E. Winger, and Bruno O. Winkler.

The regular scientific program of the Society consisted of 82 papers, numbers 24, 56, 62, 78 and 80 were read by title. The abstracts of these papers are given in the following pages. An **Author Index** will be found at the end.

W. L. SEVERINGHAUS, *Secretary*

ABSTRACTS

1. Mass absorption coefficient of the *K* shell according to the Dirac relativistic equation. LOUIS C. ROESS, *Cornell University.* (*Introduced by E. H. Kennard.*)—Taking as model an atom containing two non-interacting electrons and a fixed nucleus with charge Ze, the mass absorption coefficient is calculated using the proper functions of the Dirac relativistic equation. Z is determined so as to make the lowest energy level agree with the experimental value determined from the K absorption edge. The numerical calculation presented difficulty because of lack of tables of complex gamma functions. The relativistic coefficient is found to be from 0% to 40% smaller than the non-relativistic coefficient calculated by Nishina and Rabi, the greatest difference occurring for the heavy elements and short wave-lengths; it agrees slightly worse with experiment than the non-relativistic coefficient. The difference between theory and experiment is least for the heavy atoms, as would be expected, since for the heavy atoms (large Z) the neglected electronic interaction-field is small in comparison with the nuclear field. The variation of the relativistic coefficient with wave-length is complicated, but in the range $\frac{1}{2}\lambda_k$ to λ_k (λ_k = wave-length of K absorption edge) it is more nearly linear with λ^3 than the non-relativistic coefficient. The importance of using the relativistic equation for heavy atoms and short x-ray wave-lengths is emphasized by these results, which also show that the model chosen is too approximate, even for the heavy elements.

2. Nature of magnetic doublet in para-azoxyanisol at 122° and 128°C as determined by x-ray diffraction. G. W. STEWART, *University of Iowa.*—A difference of opinion exists as to whether the magnetic moment of para-azoxyanisol in its liquid crystalline form, 117°C to 134°C, is an induced one or is independent of the field. A magnetic field is applied perpendicular to the axis of rotation of the spectrometer and to the x-ray beam passing through the sample. The effect of the field in the diffraction halo is studied quantatively. Boltzmann's distribution law is assumed. The data are in agreement with the computations assuming the magnetic moment to be not polarized but permanent and to possess a value of 2.65×10^4 Bohr magnetons, in agreement with the results of Kast. This suggests, but does not make certain,

that a group of that number of molecules gives rise to the magnetic moment. The diffraction of x-rays at temperatures above 134° shows the disappearance of the magnetic moment, but a retention of groups otherwise similar to those just suggested. The groups causing optical anisotropy are larger and not regular enough throughout to produce coherent x-ray diffraction. These large groups are easily affected by the stirring of the liquid. The time required for orientation is easily shown by the application of an alternating magnetic field. The experiment shows the value of the direct x-ray investigation.

3. The utilization of intensity data from Laue photographs. MAURICE L. HUGGINS, *Stanford University.*—The measurement of Laue photograph intensities and the calculation of structure factors from them are discussed. Methods of correcting for differences (in intensity of the incident radiation, in absorption and in photographic effect) dependent on the wave-length, for differences (in size of the spot, in absorption and in the background of scattered radiation) dependent on the reflection angle, and for absorption (including primary and secondary extinction) dependent on the nature of the crystal, are considered and the results of preliminary measurements and calculations presented.

4. The characteristic x-ray absorption of molecules in the vapor state. J. D. HANAWALT, *National Research Fellow, University of Michigan.*—The purpose of the work here described is to provide a better understanding of the secondary absorption discontinuities which appear on the short wave-length side of the K and of the L x-ray absorption edges of many substances. The interpretation of the secondary discontinuities has been especially difficult because the absorption has not been obtained for atoms in the isolated state. In the present work the characteristic x-ray absorption spectra of numerous polyatomic and monatomic molecules in the vapor state have been photographed with a dispersion of about 5 XU/mm, and the results compared with the absorption spectra exhibited by the same substances in the solid state. The monatomic substances investigated are superheated Hg vapor, superheated Zn vapor and krypton. The polyatomic substances are the vapors of As_4, $AsCl_3$, As_2O_3, Br_2, NaBr, $HgCl_2$, Se_8, SeO_2. It is found that none of the monatomic molecules show any absorption discontinuities at distances from the main edge greater than the ionization potential of the atom. The polyatomic molecules, however, show secondary absorptions in the vapor state differing only in minor details from the absorption of the same substance in the solid state. This makes it appear that the secondary discontinuities are only observed for atoms which are bound to other atoms. If the discontinuities are to be attributed to simultaneous jumps of two or more electrons within the atom, one has yet to understand why they do not occur in isolated atoms.

5. X-ray absorption coefficients of the light elements and their relations to the various absorption formulae. S. J. M. ALLEN, *University of Cincinnati.*—The x-ray absorption coefficients of the elements have been measured with greater precision and care at $\lambda = 1.539$A and 1.934A with especial reference to the low atomic weight elements, O, C, B, Be, Li, H. It was found necessary for these to have a complete chemical analysis carried out and corrections made by the additive law to ensure resultant values of μ/ρ, for which some degree of certainty could be stated. An impurity of iron of less than 0.1 percent at $\lambda 1.539$ can have a marked effect. The values of μ/ρ, so far obtained, are compared to those predicted by the various formulae. A new formula developed by the author which was found to hold exceedingly well down to neon indicated irregularities below that point, C, N, and O certainly falling below the formula and Be and Li probably above. The same was generally true with the Z^4/A (Owens) law. The value of μ/ρ for Li at $\lambda 1.539$ extended by the λ^3 law to $\lambda 0.71$ ($K\alpha$ of Mo) gives values much less than those previously reported (Hewlett, Mazumdar) at this wave-length.

6. The upper atomic number limit of the satellites of the x-ray line $L\beta_2$. ROBERT D. RICHTMYER, *Cornell University.* (*Introduced by F. K. Richtmyer.*)—Five satellites of the line $L\beta_2$ have previously been reported for the elements in the atomic number range 40 to 51. An attempt was made to extend this range to higher atomic numbers, and to determine whether there is a limit in the atomic number scale beyond which the satellites do not exist. A Siegbahn vacuum spectrometer was used, the only departure from the usual photographic method of

x-ray spectrometry being the comparatively high voltage on the x-ray tube. The satellite $L\beta_2(a)$ was observed and measured for elements 50, 51, 52, 53, 56, 58, and 60; and two others, $L\beta_2'$ and $L\beta_2''$, only as far as element 53. For elements above Xe (54), the diagram lines (Siegbahn) $L\beta_7$, $L\beta_9$, and $L\beta_{10}$ shift their positions in the spectrum relative to $L\beta_2$ in such a way that they occupy the region just where one would expect to find the satellites $L\beta_2'$ and $L\beta_2''$, making observations difficult. The plates seem to show, however, that these satellites fade out and disappear with atomic number 53. The satellites $L\beta_2(b)$ and $L\beta_2(c)$ are not found above number 50. Throughout these extensions of their ranges the satellites, where found, obey the law that $(\Delta\nu/R)^{1/2}$ is a linear function of atomic number.

7. Upper atomic number limit of the satellites of the x-ray line $L\alpha_1$. E. RAMBERG, *Cornell University.* (*Introduced by F. K. Richtmyer.*)—The satellites of $K\alpha_1$, namely $K\alpha_3$ and $K\alpha_4$, decrease in intensity rapidly with increasing atomic number above Cu(29) and have not been reported above As(33). Their disappearance seems to coincide, roughly, with the completion of Period IV of Bohr's periodic table. Similarly the satellites of $L\alpha$, although strong at Cd(48), fade out very rapidly as the end of (Bohr's) Period V is approached. The present paper is concerned with an attempt to map, by very long exposures, these $L\alpha$ satellites in the atomic number range Sn(50) to Ce(58). There is no certain evidence of their existence above Xe(54). From Sn(50) to I(53) they fade out into a very faint, diffuse band which shows very little evidence of structure, and in which therefore the identification of the lines and their wave-length measurements are difficult. The bearing of these data on the problem of the origin of satellites is discussed.

8. Are the wave-lengths of x-ray satellites affected by chemical combination? F. K. RICHTMYER, *Cornell University.*—The "two-electron jump" theory of the origin of satellites, proposed by the author, postulates that one of the jumps should be between outer electron shells and should therefore be somewhat affected by chemical combination. That is, the difference in wave-length $\Delta\lambda$ between a satellite and its parent line should depend on the chemical state of the emitting atom. The present paper describes an attempt to detect such a shift in wave-length for the $K\alpha$ satellites of Si(14), S(16), Ca(20), Ti(22) and the $L\beta_2$ satellites of Ag(47). Except in the case of Si(14) the data are inconclusive because of the possible reduction or oxidation of the element in the target and the resulting well-known change in wave-length of the parent lines. Measurements on Si(14) were less ambiguous. Comparing the $K\alpha_{3,4}$ satellites of metallic silicon with those from Na_2SiO_3, the $\Delta\lambda$ for the silicate is 3.9 percent greater in the case of $K\alpha_3$, and 2.8 percent greater in the case of $K\alpha_4$ than for metallic silicon. These data are in substantial agreement with those of Bäcklin (Zeits. f. Physik **38**, 215, 1926). It will apparently be necessary to study fluorescence spectra to avoid spurious effects of chemical reduction in the target.

9. Interpretation of x-ray satellite lines. R. M. LANGER, *Massachusetts Institute of Technology.*—Quantum mechanical calculations show that double electron jumps involving two electrons in different shells would give lines too faint to account for observed x-ray satellites. A theory can be given for single electron jumps in doubly ionized atoms which would give lines of much greater intensity and which would be compatible with the experimental results of Richtmyer and Taylor, and DuMond and Hoyt. According to this theory the $K\alpha$ satellites α', α_4, α_3, α_5, α_6 of the elements from Na on, are due to the transitions

$$(1s)(2s)(2p)^6\ {}^1S - (1s)^2(2s)(2p)^5\ {}^1P \ldots\ (\alpha')$$
$$(1s)(2s)(2p)^6\ {}^3S - (1s)^2(2s)(2p)^5\ {}^3P \ldots\ (\alpha_4)$$
$$(1s)(2s)^2(2p)^5\ {}^3P - (1s)^2(2s)^2(2p)^4\ {}^3P \ldots\ (\alpha_3)$$
$$(1s)(2s)^2(2p)^5\ {}^1P - (1s)^2(2s)^2(2p)^4\ {}^1S \ldots\ (\alpha_5)$$
$$(1s)(2s)^2(2p)^5\ {}^1P - (1s)^2(2s)^2(2p)^4\ {}^1D \ldots\ (\alpha_6).$$

There are five transitions to be expected and five are observed. Moreover the relative intensities come out in agreement with experiment. Accurate calculations of the separations between lines cannot at present be made because exact wave functions are not known. The

best available wave functions give separations about 50 percent off. The present theory can be extended to explain the structure of absorption edges and the shift of absorption edge with valence.

10. A check on the lattice constants and axial ratios of stibnite. JOHN G. ALBRIGHT, *Case School of Applied Science.*—Dana (Textbook of Mineralogy) classifies stibnite as orthorhombic with axial ratios 0.9926:1:1.0179. Gottfried (Zeitschrift für Kristallographie **65,** 427–434, 1927) gives the axial ratios as 0.992:1:0.338 and the lattice constants as $a=11.39$A, $b=11.48$A, $c=3.89$A, making the value for the unit cell along the c axis about one third of that indicated by Dana's values. In view of Dana's reputation for accuracy it was thought desirable to check the determinations of Gottfried. X-ray diffraction and reflection photographs give values for the lattice constants of $a=11.29$A, $b=11.45$A, $c=3.87$A, making the axial ratios 0.986:1:0.339, which agree very well with the values given by Gottfried.

11. X-ray analysis of cold rolling and recrystallization in steel. C. NUSBAUM, *Case School of Applied Science.*—A careful and extensive study, by means of Laue photographs, has been made of the effect of cold rolling on low carbon steel and the subsequent heat treatment necessary for its complete removal. The changes due to increasing degrees of cold rolling may be considered as taking place in three stages (1) introduction of internal stresses as indicated by radial asterism, (2) the fragmentation of the individual crystals, and (3) the increasing degree of preferred orientation of the crystal fragments. The necessary temperature in the subsequent heat treatment for the complete removal of the effect of cold rolling is a function of the degree of the cold work. However, recrystallization is necessary for the complete removal of preferred orientation.

12. The "spread" as a measure of deviation in physical measurements. ELLIOT Q. ADAMS, *Lamp Development Laboratory, Nela Park.*—In order to compare results of incandescent lamp tests expressed in terms of the spread (maximum difference) observed in sets of various numbers of lamps, it was necessary to calculate factors to convert these results to a comparable basis. The average deviation of a single observation was chosen as the basis of comparison. Assuming a Gaussian distribution of errors, the factors have been calculated by mathematically approximate methods, and may be expressed by the semi-empirical formula: Spread/(av. deviation) $=f(n)=(5.304-2.11/(0.47+\lg n))(\lg n)^{1/2}$ with an error not exceeding 0.01 in the factor. This error is negligible in comparison with the unavoidable error in determining by any method the average deviation in a set of fewer than 10^5 observations, i.e., in practically all physical measurements. While it may be shown mathematically that the average deviation so computed is less precise than that computed from the sum of the residuals, or *a fortiori* of their squares, the difference seldom exceeds the probable error of the more refined measures. The labor of computation is so much less than that of the more precise methods that an expression of the internal consistency of *all* results of physical measurements may reasonably be required.

13. The wave-mechanical theory of radiation. E. H. KENNARD, *Cornell University.*—A complete theory can easily be developed in terms of traveling plane waves instead of standing oscillations; such a form should be especially useful in dealing with phenomena which like the Compton effect involve motion. Replacing the usual Fourier integral by a series we write for the classical vector-potential of the radiation field, $A=\Sigma(i)(a_i l_i' \cos\theta_i + a_i'' l_i'' \sin\theta_i)\,\Delta\nu\Delta\omega$ where $\theta_i=2\pi\nu_i(t-gx_i)$, $c=1/g$ being the speed of light, x_i distance along the ray, l_i' and l_i'' two perpendicular unit vectors and $\Delta\omega$ an element of solid angle. As coordinates and momenta we take $Q=\beta_1 a' \cos 2\pi\nu t$, $P=\beta_1 a' \sin 2\pi\nu t$, and $Q=\beta_1 a'' \sin 2\pi\nu t$, $P=-\beta_1 a'' \cos 2\pi\nu t$, $\beta_1^2=c\Delta\nu\Delta\omega/2\nu$; the energy is then $W=\Sigma(\sigma)\pi\nu_\sigma(Q_\sigma^2+P_\sigma^2)$, and $\boldsymbol{A}=\Sigma\boldsymbol{A}_\sigma=\Sigma\beta_\sigma l_\sigma(Q_\sigma\cos\theta_\sigma+P_\sigma\sin\theta_\sigma)$ where $\theta_\sigma=2\pi g\nu_\sigma x_\sigma$, $\beta=2\nu\beta_1/c$. We now replace P_σ by $h/2\pi i\partial/\partial Q_\sigma$ and form the Schrödinger time equation, adding in the Hamiltonian for a non-relativistic free electron simply $1/2m(\nabla-e/c\Sigma\boldsymbol{A}_\sigma)^2$. The motion of a packet is easily followed; formulas almost classical in form are obtained for its centroid, with the operators $-\Sigma\partial\boldsymbol{A}_\sigma/\partial x_\sigma$ and $\Sigma\nabla\times\Sigma\boldsymbol{A}_\sigma$ acting as electric and magnetic field-strengths. The acceleration vanishes when the field is in its normal

or any other pure quantum state, showing that the "zero-point" infinite energy does not imply the existence of a physical electromagnetic field.

14. On the mechanism of light absorbtion in solid bodies. J. FRENKEL, *Visiting professor from Leningrad, University of Minnesota.* (*Introduced by H. A. Erikson.*)—Starting from the analogy between a crystal and a molecule, it is shown that the electronic excitation, forming the first step in the process of light absorbtion, is not confined to a particular atom, but is diluted between all of them in the form of "excitation waves," similar to sound waves which are used to describe the heat motion in the same crystal. Owing to the interaction between the atoms the excitation state is split up into substates whose number is equal to the number of atoms n (excitation multiplet). By superposing several excitation waves "excitation packets" can be constructed representing the travelling of the excitation state from one atom to another. To each excitation (sub.) state there corresponds a definite crystal structure (lattice constant, vibration frequencies) slightly different from that of the normal one, and giving rise to slightly different vibrational states. This influence of the excitation on the vibrational states provides an indirect coupling between them, which allows the excitation energy to be shared between a few hundred heat-oscillators with practically no direct coupling (nor anharmonicity) in a radiationless transition which forms the second state of the process of light absorbtion.

15. Interchange of translation, vibration, and rotation energy. CLARENCE ZENER, *Harvard University.*—A modification of the Born collision method is used to calculate the effective cross-sections of inelastic collisions of the first and second kind between atoms and molecules. The unperturbed Hamiltonian is taken to be the exact Hamiltonian averaged over the internal coordinates of the molecule. The internal motions of the molecule is treated as the perturbation that results in a transfer of energy. The sharpness of the collisions is approximately obtained from the mean ionization potentials of the two colliding systems. The small probability of transfer of vibrational and translational energy arises from the duration of the collision being greater than the time of oscillation. In general, the effective cross-section for a collision of the second kind is comparable to the kinetic theory cross-section only when a frequency of the molecule is comparable to a frequency associated with the combined system of molecule and atom.

16. Orbital valency. JAMES H. BARTLETT, JR. *University of Illinois.*—The problem of interaction of two identical atoms, each with one p valence electron, has been investigated. The total system has originally a twelve-fold degeneracy, and a first order perturbation calculation is made, using a method analogous to that of Kemble and Zener for the excited states of the hydrogen molecule. This enables one to give an estimate of the relative positions of the resulting molecular states as a function of the internuclear distance. A simple atomic wave function similar to those employed by Zener (with no radial nodes) has been used in the present work to facilitate the calculations. Complete potential energy curves have now been obtained, and agree in general with the results reported in a letter to the Physical Review **36,** 1096 (1930).

17. Directed valence in polyatomic molecules. J. C. SLATER, *Massachusetts Institute of Technology.*—By means of wave mechanics one can draw conclusions regarding valence in polyatomic molecules, finding in particular that the different shared electron bonds from a single atom tend to be at definite angles to each other. The two bonds in atoms like oxygen, and the three in nitrogen, tend to be mutually perpendicular, while in carbon a tetrahedral structure is indicated. These conclusions in the first two cases rest on the nature of the wave function for a p electron: the three types of p electron may be considered to have densities large along three mutually perpendicular directions. With carbon, one must combine these three with an s electron to produce tetrahedral valences. The conclusions can be supported by a wide range of experimental facts, from the structure of simple inorganic molecules, metals, and organic compounds.

18. Polarizabilities and intra-atomic energies of hydrogen and helium. JOHN G. KIRKWOOD, *Massachusetts Institute of Technology.* (*Introduced by J. C. Slater.*)—A method of calcu-

lating polarizabilities and intra-atomic energies has been developed. An approximate separation of variables in the original wave equation is effected. From the approximate wave function which is obtained, a more exact one is constructed with the use of the variation principle. The polarizability and energy of two atoms at large distances have been calculated for hydrogen and helium.

19. On the Michelson-Morley-Miller experiment. N. GALLI-SHOHAT, *Mount Holyoke College.*—At the meeting of the American Physical Society held in Washington in April, 1930, it was suggested by the writer that Professor Miller's effect can be explained by means of the effect observed by Esclangon. This further enables us to explain why Professor Michelson in the last repetition of his experiment did not observe any effect. In fact, the displacement of the fringes due to the effect of Esclangon (rotation of the whole interference pattern) depends only upon the orientation relative to the motion of the solar system of that part of the path of light in the interferometer, which goes from the last reflection directly into the eye of the observer. In the arrangement of apparatus used by Professor Michelson, this path was made stationary, being directed *along the axis of rotation.* Thus, the revolution of the interferometer around this axis *could not change* the orientation of this path in space; hence, *no effect can be expected.* While in his first arrangement, which was used also by Professor Miller, this path lies *in the plane* of the interferometer, hence, a change due to revolution and a displacement of the fringes.

20. Change in mass-weight ratio. PETER I. WOLD AND EARLE M. BIGSBEE, *Union College.*—The late Charles F. Brush carried on experiments which led him to conclude that the weight of a metal may change when strained, giving a change in the ratio of mass to weight. His experimental technique seemed to preclude the obvious sources of errors which might be urged as explanation of his results. The matter is of sufficient importance to our theories of gravitation to justify checking and at his request weighings were made on certain alloys prepared by him. The procedure was practically the same as described in his paper in Proceedings of the American Philosophical Society (Vol. 63, 1925, p. 36). Weighings taken on various specimens showed losses in weight when the specimen was compressed and a nearly complete recovery when the stress was removed. The changes were substantially in excess of balance errors. The losses were less than found by Brush and he considered this as due to annealing during the time between the preparation of the sample and its weighing. The shorter this time the larger were the observed effects. In the last sample studied, where elapsed time was shortest, the losses amounted to one part in 130,000. The work may be considered as confirming that of Brush. The suggestion that the effects are due to changes in the amount of adsorbed gases does not appear to be a sufficient explanation.

21. Properties of single crystal magnesium. P. W. BRIDGMAN, *Harvard University.*—Pure magnesium, which I owe to the Aluminum Company of America, was prepared in single crystal form by slowly lowering out of a vacuum furnace iron molds filled with the melted metal. The crystal structure of magnesium is known to correspond to the close packed hexagonal arrangement of spheres. It is therefore to be expected that the properties will not vary greatly with direction. This turns out to be true for the compressibility, for which was found:

Parallel to the axis, at $30°-\Delta l/l_0 = 9.842\times10^{-7}p-6.51\times10^{-12}p^2$
at $75°-\Delta l/l_0 = 10.154\times10^{-7}p-7.78\times10^{-12}p^2$.
Perpendicular to the axis, at $30°-\Delta l/l_0 = 9.845\times10^{-7}p-9.19\times10^{-12}p^2$
at $75°-\Delta l/l_0 = 9.659\times10^{-7}p-6.95\times10^{-12}p^2$.

Pressure is expressed in kg/cm², and the pressure range is 12000.

The electrical resistance, however, does not satisfy expectations. At 22°.5 the specific resistance is 3.89×10^{-6} parallel to the axis, and 4.60×10^{-6} perpendicular to it. Not only does the resistance vary materially with direction, but in almost all other non-cubic metals the resistance is greater parallel to the axis. The average pressure coefficient to 12000 was found to be 4.35×10^{-6} parallel to the axis, and 4.62×10^{-6} perpendicular to it. The temperature coefficient of resistance at atmospheric pressure between 0° and 100° was 0.00523 and 0.00428 respectively.

22. Transverse heat effect in single crystal bismuth plates. H. P. STABLER, *Harvard University.*—The dependence of the transverse heat on the orientation of the crystallographic axis has been studied in single crystal bismuth. The metal was of three different varieties (of which one was specially prepared electrolytic bismuth) all having high temperature coefficients of resistance and giving identical results. The crystals were grown by a modification of Kapitza's method in the form of uniform rectangular plates, about 15×2.2 mm cross-section, and perfect over a length of from 4 to 16 cm. Measurements made on twenty-eight plates covering the entire range of orientation show clearly that the Thomson symmetry relation for the tranverse heat, $[T(\theta)=(P_{\parallel}-P_{\perp})\sin\theta\cos\theta]$, is not satisfied. The ratio $(T(\theta)/\sin\theta\cos\theta)$ plotted against $\sin\theta\cos\theta$, instead of being constant, varies in a roughly sinusoidal manner, with the extremes at 15° and 75° differing by $24\%\pm5$. These values are 14.2 and 18.0×10^{-3} watts respectively, and at 45°, 15.9. Bridgman, and Fagan and Collins have shown that the longitudinal Peltier effect also, in bismuth, deviates from the analogous Thomson relation. Ehrenfest's recent treatment of these phenomena in crystals arrives at the Thomson relations, and thus his treatment, though general, is not sufficiently comprehensive to account for these experimental results.

23. Liquid flow through porous unsaturated mediums. L. A. RICHARDS, *Cornell University.*—When a liquid is absorbed by a porous medium and the medium is unsaturated the pressure within the liquid is less than atmospheric pressure and is determined by the curvature of the air-water interface. Under such circumstances flow of the liquid through the medium is caused by gravity and pressure gradients within the liquid. Analogous to electrical currents in metals, this flow may be expressed in terms of the product of a potential gradient and a conductivity factor. For the capillary case, however, the conductivity is a function of the potential which in turn is a function of the liquid content of the medium. By means of specially constructed porous cells the conductivity of water through clays, soils and sands has been measured at various potentials. These data furnish a basis for a quantitative study of the motion and equilibrium distribution of water in such mediums.

24. Determination of frequency and damping of resonating circuits. J. TYKOCINSKI-TYKOCINER, *University of Illinois.*—It was found as a further result of studies of thermionic oscillators (Phys. Rev. **33**, 634 (1929); and Univ. of Ill. Eng. Exp. St. Bul. No. 194) that periodic variations of constants of a coupled circuit produce periodic variations of plate and grid current. This property of oscillators was investigated and applied for the determination of frequency and damping of circuits whose location or other conditions do not allow the insertion of a variable condenser, variometer or resonance indicator. The circuit is coupled with a calibrated circuit energized by a thermionic oscillator tube and with an aperiodic circuit, whose reactance or resistance may be varied periodically by means of an electromagnetic tuning fork, buzzer or by superposed a.c. When the oscillator is being tuned, variations of the plate and grid current are produced, which show a periodicity corresponding to that of the tuning fork or a.c. and a transient amplitude passing through two maxima and a sharp minimum placed between them. The *M*-curve of effective current values thus obtained is a curve of derivates of the Bjerknes resonance curve. The minimum coincides with the fundamental frequency. The interval separating the two maxima is proportional to the decrement of the measured circuit. The maxima and minimum of the *M*-curve are audible in a telephone receiver. The complete curve is obtained by thermoelectric or thermionic instruments connected to amplifiers. The method was applied to closed circuits and antennae at frequencies from 100 to 100,000 kc.

25. The amplification of small direct currents. L. A. DUBRIDGE, *Washington University, St. Louis.*—A series of tests has been made by the author, under the supervision of Dr. Hull at the General Electric Laboratories, to investigate the possibilities of using a newly developed four-element thermionic tube, the FP-54 Pliotron, (described by Metcalf and Thompson, Phys. Rev. **36**, 1489 (1930)) in place of an electrometer in the measurements of very small direct currents. Simple circuits of standard types were found suitable and a wide range of sensitivity obtained. (1) With a single-tube circuit, using a Type R galvanometer and an input

resistance of 10^{16} ohms, a current sensitivity of 10^{-14} amp/mm is readily obtained. (2) Greater stability is attained by using a balanced two-tube circuit, with which a sensitivity of 10^{-16} amp/mm can be reached. (3) By "floating" the two grids of this circuit and using the "rate of drift" method of measurement, it was found that currents as small as 5×10^{-18} amp could be detected. (4) To enable the output to be read on a microammeter a second stage of amplification was employed. A deflection of 4 micro-amp. was obtained for an input current of 10^{-13} amp. The circuits are all more stable and simpler to operate than an electrometer of equal sensitivity, and the highest attainable sensitivity is greater than for any type of electrometer except the Hoffman.

26. Studies in non-linear circuits. CHAUNCEY GUY SUITS, *General Electric Company, Schenectady.* (*Introduced by A. W. Hull*).—The fundamentally important series inductance, capacitance, resistance circuit

$$L'(i)\frac{di}{dt}+\frac{1}{C(i)}\int idt+iR(i)=f(t), \tag{1}$$

where the parameters are functions of the current, is discussed. The frequent occurrence and great practical importance of circuit elements which depend upon the current are noted. The particular cases of the series and parallel circuit with linear resistance, linear capacitance, and a non-linear iron-core inductance are studied in detail. For the *series circuit* it is shown that the abrupt rise in current with increase in voltage at a certain critical voltage for the circuit may be identified as a quasi-resonance condition, called *non-linear resonance*. The condition for resonance in the linear circuit,

$$-L'\frac{di}{dt}=\frac{1}{C}\int idt, \tag{2}$$

is generalized as

$$-L'(i)\frac{di}{dt}=\frac{1}{C(i)}\int idt \tag{3}$$

for non-linear cases. The relation (3) is satisfied in the steady state *during a portion of each cycle*, wherein the peak current may be calculated from Ohm's law. For the *parallel* circuit *non-linear resonance* similarly obtains, and is associated with a decrease in total effective current with increase in voltage (r.m.s.), a property unique in circuits. The fundamental analogy between the behavior of linear circuits to changing frequency and non-linear circuits to changing voltage follows from the predominating voltage dependence of impedance for the non-linear iron-core inductance. The paper will be accompanied by demonstration apparatus if time permits.

27. The effect of the temperature dependence of the work function on A and b in Richardson's equation. J. A. BECKER AND W. H. BRATTAIN, *Bell Telephone Laboratories, Inc., New York.*—The most general form of Richardson's equation is

$$i=AT^{-1/2}\epsilon^{\int(L_p/RT^2)dT} \tag{1}$$

where L_p represents the energy added to the system when one mole of electrons is "vaporized" at constant pressure. This equation follows necessarily from the first and second law of thermodynamics and from the generally accepted assumption that the electron vapor behaves like a perfect gas. In order that

$$i=AT^2\epsilon^{-b_0/T} \tag{2}$$

it is *necessary* that

$$L_p=b_0R+5RT/2 \tag{3}$$

and *to assume that b_0 is independent of T*. $5RT/2$ represents the kinetic energy of the electron gas plus external work done per mole at constant pressure. It is generally assumed or deduced that the electrons in the metal receive negligible energy when T is increased. In that case, $L_p-5RT/2$ represents work done per mole against various electrical forces. Call this bR. If bR depends on T, (1) becomes

$$i = AT^2 \epsilon^{\int (b/T^2)\,dT}. \tag{4}$$

If $b = b_0 + \alpha T$

$$i = AT^{2+\alpha} \epsilon^{-b_0/T}. \tag{5}$$

If the work function varies linearly with T, we conclude: 1. equation (5) replaces (2) which is invalid; 2. the mean slope of $\log i - 2 \log T$ vs. $1/T$ is $b_0 + \alpha T$ and not b_0; 3. the intercept of this plot is $\log (A \epsilon^{\alpha} T^{\alpha})$ and not $\log A$ or $\log (A \epsilon^{-\alpha})$.

28. Conductivity of oxide cathodes. N. H. WILLIAMS AND W. S. HUXFORD, *University of Michigan.*—The conductive properties of oxide coatings used in the equipotential cathode type of radio tube have been investigated. The inner nickel sleeve served as one electrode, the second being a nickel strip in contact with the outer surface of the oxide. Currents through the coating as measured at constant potential vary with the frequency of the applied electromotive force. A decrease in conductivity of about forty percent occurs when the freqeuncy is changed from 1500 to about 10,000 cycles per second. The decrease starts at lower frequencies for higher values of applied potential. These results indicate a transfer of electrical charges through the coating by ionic conduction, the process being inhibited at the higher frequencies. A method of estimating the relative thermionic activities of core metal and oxide surface is suggested. Fluctuations in the current through the coating were measured on an amplifier tuned to various frequencies from 200 to 40,000 cycles per second. An abnormal increase in "shot" voltage was found for frequencies below 10,000 cycles. This result is believed to confirm the hypothesis that positively charged ions are neutralized in the space charge produced by electrons which are emitted thermionically from the activated surface of the core metal.

29. The electrical polarization of electrets. MAURICE EWING, *Lehigh University.*—The internal electrical polarization of an electret was determined by breaking a piece of the electret along a plane normal to the direction of polarization and measuring the charge per unit area which appeared on the newly-formed surfaces. The polarization for this particular electret was found to be 2.0 ± 0.2 esu/cm^2. The theory of Adams (Frank. Inst. J., **204,** 469 (1927)) seems to require that the polarization in an electret be of the order of 10^5 esu/cm^2.

30. Electrical characteristics of a viscous mineral insulating oil as functions of temperature and frequency. H. H. RACE, *General Electric Co., Schenectady.*—Data recently taken on the dielectric loss and the dielectric constant of good mineral insulating oils lead to the following conclusions: (a) At constant temperature the dielectric constant decreases by only a few percent as the frequency is increased from sixty to two million cycles per second. (b) At constant frequency the dielectric constant decreases with increased temperature and this change appears to be proportional to the decreasing density of the oil. (c) For a given temperature there is a critical frequency such that for all lower frequencies the A.C. loss is independent of the frequency and for all higher frequencies the loss increases with the frequency. Within the first frequency range the mechanism of D.C. conduction and of A.C. loss appear to be the same, and both are probably due to the migration of charged ions or larger particles in the oil. Within the second range, the loss per cycle, (after that resulting from D.C. conduction has been subtracted), shows resonance characteristics as a function of either temperature or frequency. (d) The higher the temperature, the higher the critical frequency below which the A.C. and D.C. losses are the same. Power factors as high as 1% have been observed under conditions for which the loss resulting from conduction would be negligible. These data have been studied from the point of view of Debye's theory of polar molecules, and a qualitative agreement has been found.

31. Dielectric constants of certain organic compounds. W. R. PYLE, *The Ohio State University.*—The dielectric constant of an organic compound is thought to be allied with its other physical properties such as solvent power and molecular complexity. Probably the future will reveal a more definite correlation between the dielectric constant and the other physical properties of a compound. The nulled heterodyne method of measurement of dielectric constants was made possible by the advent of the triode valve and it is employed in this work. For room temperature and at a frequency of 85.8 kilocycles the dielectric constant was determined for

each of the following: benzene, carbon tetrachloride, chloroform, cinnamic aldehyde, ethyl ether, methyl cyclohexane, methyl o-nitrobenzoate, nitrobenzene, oxalyl chloride, n-propyl ether, iso-propyl ether, o-xylene, m-xylene and p-xylene. The temperature coefficients of the dielectric constant for ortho-, meta-, and para-xylenes were determined over a range of about 25°C for both the linear formula and Abegg's formula. It seems reasonable to believe that the values of the dielectric constants determined in this work are relatively as accurate as the purity of the organic compounds.

32. Maintaining direction in flight. JAMES D. TEAR, *General Electric Co., Schenectady, N. Y.*—Accelerations due to changes in course cause the aircraft compass to be responsive to the vertical component of the earth's magnetic field and to be misleading as a direction instrument. North courses cannot be flown without other reference means. The potential generated by an electromagnetic compass is a function of the course setting θ, the course error $\Delta\theta$ and the product of angular velocity and speed or the angle of bank ϕ. A gyroscopic device, the sensitivity of which is controlled by the course setting mechanism, supplies a potential proportional to sin ϕ and cos θ compensating the acceleration error. An additional angular velocity effect independent of course is added. A null effect then requires an angular velocity toward the chosen course proportional to angular displacement, the condition for aperiodic steering. The adequacy of the system for maintaining direction in clouds has been verified in a series of experiments in which the rudder angle was automatically made porportional to the algebraic sum of the potentials in the compass circuit.

33. A method of weather forecasting. R. C. COLWELL, *West Virginia University.*—It has been shown before that when a high pressure area covers both Pittsburgh and Morgantown, the day signal from KDKA is stronger than the night signal, while for a low pressure area, the night signal is the stronger. Hence the ratio of the day to the night energy received from KDKA at Morgantown will give some indication of the atmospheric conditions between the two cities. In this method of forecasting, a fading curve is taken for about one hour before sunset and three hours after sunset. The area is measured with a planimeter and the ratio of the day to night energy is calculated for each day. If this ratio is greater than one, fair weather is indicated; whereas, if the ratio drops to one half, a storm is approaching. In addition to this ratio, barometer readings are taken and wind directions observed. A storm area passing north of Morgantown will cause a low barometer and a south wind. If the storm center passes to the south, the energy ratio from a station to the north is no longer reliable and readings must be taken upon a station to the south.

34. Photoelectric properties of composite surfaces at various temperatures and potentials. DIMITER RAMADANOFF, *Cornell University.* (*Introduced by Ernest Merritt.*)—A large number of experiments were carried out with Ba photoelectric cells to determine the variation of photoelectric current with temperature and plate potential. In all cases the photoelectric current increased greatly at the higher temperatures, and reached maximum at 740°C. At this temperature the thermionic current was limited by space charge. By illuminating the photoelectric cell with interrupted light, the intensity of which was varied sinusoidally, it was possible to measure the photoelectric current with a new method which incorporates the use of a transformer coupled amplifier and a Bedell-Reich stabilized "Oscilloscope." With this apparatus the thermionic current, and sluggish currents which may be due to light in a secondary way, were completely eliminated and only the true photoelectric currents were measured. In this way a curve was obtained which represents the relation of photoelectric current vs. temperature at a constant applied voltage. This curve shows two distinct maxima at 560°C and 740°C the first of which is not observable with a galvanometer if constant illumination is used.

35. Correlating the selective photoelectric effect with the selective transmission of electrons through a cathode surface. A. R. OLPIN, *Bell Telephone Laboratories, Inc.*—The results of Fowler and others with respect to the penetration of α-particles into a model nucleus suggested the possibility of explaining the selective photoelectric effect by the selective transmission of electrons of a definite velocity through the cathode surface. These electrons must be

associated with waves of such length that they will form standing waves between abrupt potential discontinuities of like sign on the cathode surface. The existence of such a potential valley may be reasonably postulated, particularly for surfaces consisting of a layer of electronegative atoms or molecules sandwiched between electropositive layers. By interpreting the width of the valley to be the distance between the nuclear boundaries in successive electropositive layers and substituting these for d in the easily derivable equation $\nu_{max.} = n^2h/8md^2$ [or $d = 0.0551\ \lambda_{max.}^{1/2}$ Angstroms, for the case of $n = 1$], an extremely close correlation with experimental facts results. All the observed selective maxima in spectral photoelectric response curves for the hydrides, oxides and sulphides of the alkali metals have been checked by this equation with a higher degree of accuracy than has been obtained by any other theory.

36. Physical detectors of "Mitogenetic Radiation." OTTO GLASSER AND V. B. SEITZ, *Cleveland Clinic Foundation, Cleveland, Ohio.*—Experiments of Alexander Gurwitsch and coworkers in 1924 showed that some form of radiation from growing and dividing cells of various plants and tissues produced increased mitosis in other cells. Since then this observation has been experimentally substantiated by numerous other workers. An attempt is described to detect and classify these "mitogenetic radiations" by physical means and some results of these experiments are reported.

37. Thermoluminescence excited by exposure to radium. FRANCES G. WICK, *Vassar College.*—The experiments described in this paper were made at the Institute for Radium Research in Vienna and the method of observation is one which has been used there by Dr. Karl Przibram. Calcium sulphate plus manganese and specimens of fluorite were exposed to radium and the thermoluminescence excited by this exposure was measured by heating the specimens in front of a photo-electric cell connected with a Wulf electrometer. Observations were made from the beginning of heating until the light was exhausted. Subjecting the specimens to a pressure of 10,000 Kg/cm² either before or after exposure to radium was found to change the intensity of the light emitted. Calcium sulphate plus manganese shows a single maximum of intensity as the temperature rises. The effect of pressure applied either before or after exposure to radium is to diminish the height of this maximum. Powdered fluorite previously heated to remove all natural thermoluminescence, shows, after exposure to radium, a number of sharp maxima due to different rare earth impurities. These maxima are lowered as a result of pressure. A broad diffuse band in the blue upon which the sharp bands are superimposed is made stronger as a result of pressure.

38. Significance of wave-length in color vision. C. A. RINDE, *College of the Pacific.*—Helmholtz and Koenig showed all color sensations to be reproducible by mixing light of three specific wave-lengths. Ladd-Franklin suggested red and green, blue and yellow as primary; each pair belonging to a single sensitive mechanism. The author's measurements of the retinal areas sensitive to homogeneous light selected from various regions of the grating spectrum indicate that the four areas exist and are independent. The approximate wave-length range to which each is sensitive has been measured, and an additional area sensitive only to the shorter wave-lengths has been found.

39. Appearance of color bands in films of sputtered tin. LESTER I. BOCKSTAHLER AND C. J. OVERBECK, *Northwestern University.* Small circular cathodes of tin are used to sputter films on glass. These films show concentric rings of color similar in appearance to Newton's rings. When viewed with monochromatic light, the rings are alternately light and dark. In white light the films show several cycles of the colors of the visible continuous spectrum. The growth of a set of rings, when viewed with reflected white light, begins with the appearance of a blue center a few seconds after the discharge is started. This center gradually passes through a cycle of colors of increasing wave length until it is red. With the appearance of each new center color all preceding colors move outward and form surrounding bands. The red center then merges into blue and the cycle is repeated. The rate of growth of a set of bands depends on the nature of the gas as well as on its pressure and the current density. Under a given set of conditions the change of color of the center and the addition of another set of color bands takes place with very definite regularity. Work is in progress to determine the chemical nature of these films and the cause of the colors.

40. The transmission of visible light through fog. H. G. HOUGHTON, *Round Hill Research Division, Massachusetts Institute of Technology (Introduced by J. A. Stratton).*—Measurements have been made on the transmission of visible light through artificial fog which was produced by condensing low pressure steam. Curves for various densities of fog were plotted and found to have definite maxima at about 4900A. The relation between fog density and the transmission of light was found to be practically linear for all wave-lengths in the visible spectrum. The maxima obtained are not in agreement with the results of other investigators but it is thought that this is due to a difference in the particle size of the fogs. Measurements indicated that the particles of the fogs used were considerably smaller than those of the fogs employed by other experimenters.

41. Theoretical discussion of the transmission of light through fog. J. A. STRATTON AND H. G. HOUGHTON, *Massachusetts Institute of Technology.*—The transmission of light through fog has been studied from a theoretical standpoint in an attempt to explain the experimental results described in another paper. The treatment is based on the work of Debye, Mie, Jobst and others on the pressure of light and on the colors of colloidal solutions. The fog particles are considered to be perfect dielectric spheres having an index of refraction of 1.33 and a permeability of unity. The coefficient of absorption, which is a function of particle diameter, is obtained by direct summation of Jobst's expression. By proper selection of particle diameter a theoretical curve is arrived at which fits the experimental curve quite closely. This particle size checks the measured value within the accuracy of the measurements. The transmission of light through fog having larger particles may be readily computed in the same manner.

42. Ultraviolet energy radiated by General Electric type S-1 lamps in quartz bulbs. B. T. BARNES, *Nela Park Laboratory, Cleveland.* The energy flux density of the principal ultraviolet lines from General Electric S-1 lamps in fused quartz bulbs has been measured. The latter are made somewhat smaller than the glass bulbs so that with normal operation the temperature of the mercury pool will be the same in the two cases in spite of the lower absorption of the quartz in the infra-red between 2 and 4μ. The gain in intensity by use of quartz bulbs is even greater than expected. With quartz bulbs the lines at 2650 and 2537A are nearly as strong as those around 3000A.

43. The General Electric photoflash lamp. W. E. FORSYTHE AND M. A. EASLEY, *Nela Park Laboratory, Cleveland.* The bulb of the new photoflash lamp contains about fifty milligrams of aluminum foil that has a surface of about three hundred sixty square centimeters. This lamp can be operated from a one and one half volt storage battery or from a one hundred fifteen volt line. As the lamps are now constructed they start about two hundredths of a second after they are turned on and from the beginning of the flash to the maximum is about sixteen thousandths seconds while the whole flash lasts about six hundredths seconds. The maximum flux amounts to well over one million lumens.

44. Recent Developments in Architectural Acoustics. PAUL E. SABINE, *Riverbank Laboratories.*

45. Some Physical Characteristics of Speech and Music. HARVEY FLETCHER, *Bell Telephone Laboratories, Inc.*

46. Concerning Some of the Problems Encountered in Recording and Reproducing Photographic Sound Records on Moving Picture Film. CLARENCE W. HEWLETT, *General Electric Company.*

47. Magnetostriction measurements using a heterodyne beat method. A. B. BRYAN AND C. W. HEAPS, *Rice Institute.*—The apparatus previously used in measuring discontinuous changes in length accompanying the Barkhausen effect in nickel has been employed for gross magnetostriction measurements in nickel and iron and in magnetite, hematite and bismuth crystals. Length changes in a direction parallel to the applied magnetic field are measured. The results for nickel and iron are similar to those previously obtained. Magnetite expands

for two orientations and contracts for a third and shows no hysteresis. Hematite shows a small expansion for each of two orientations. For bismuth a field of 2160 gauss produces no measurable change in length. It is estimated that $\Delta L/L$ is less than 2.2×10^{-9}. Additional measurements are to be made with larger magnetic fields and higher sensitivity.

48. Variation of magnetic susceptibilities with temperature in Sm^{+++} and Eu^{+++}. AMELIA FRANK, *University of Wisconsin.*—Calculation of susceptibilities in Sm^{+++} and Eu^{+++}, previously made at room temperature only (J. H. Van Vleck and A. Frank, Phys. Rev. **34**, 1494 (1929)) were extended to include values over a temperature range 14°K–1000°K using the theoretical expression previously given (l.c.). The value of the temperature coefficient $(1/\chi)(d\chi/dT)$ at 300°K was found to be -0.00187 for Eu^{+++} and only -0.00032 for Sm^{+++} in contrast with the normal Curie value -0.00333. These values are in satisfactory agreement with existing experimental data. Cabrera finds -0.002 for Eu^{+++} while Freed and other observers report values in the neighborhood of -0.0006 for Sm.$^{+++}$ The coefficient for Sm^{+++} is so abnormally small that accurate percentage agreement cannot be expected. The computed values show that Sm^{+++} should exhibit a curious behavior in that, while at low temperatures the susceptibility decreases quite rapidly with an increase in temperature, a minimum is reached at about 400°K.

49. On the theory of magnetic susceptibilities of salts of the iron group. J. H. VAN VLECK, *University of Wisconsin.* It is well known that the susceptibilities observed for these salts, in marked contrast to those of the rare earths, do not have the theoretical values for free ions, but instead conform to a formula $\chi=N(he/2\pi mc)^2S(S+1)/3kT$ obtained by assuming that only the spin S of the paramagnetic ion contributes freely to the susceptibility. As emphasized by Stoner, (Phil. Mag. **8**, 250), this demands that inter-atomic forces quench the magnetic effect of the orbital angular momentum, both in solids and solutions. The present paper aims to show that these forces can really do this. Following Bethe and Kramers, they may be approximately represented by a potential V whose series development usually begins with second order terms $Ax^2+By^2+Cz^2$. If $|(A-B)\bar{x}^2|\gg kT$ etc., or in general if V has no more than rhomboidal symmetry and is large compared to kT, these inter-atomic forces really quench the orbital moment. For the spin to be free, however, one must have $(h\Delta\nu_M)^2/h\Delta\nu_V\ll kT$, where $h\Delta\nu_M$ and $h\Delta\nu_V$ are respectively of the order of magnitude of the multiplet intervals for free ions and of the dissymmetry in V. These conditions require that $h\Delta\nu_V$ likely be of the order 0.1 to 1 volt. This agrees qualitatively with the coloring of iron salts in solution, which indicates that the ion is held in complexes whose binding energy is about 1 volt.

50. Magnetic susceptibilities of some binary alloys. F. L. MEARA, *Ohio State University.*—Gouy's method for measuring susceptibilities has been used to determine the susceptibilities of six series of binary alloys, tin-thallium, cadmium-zinc, antimony-cadmium, antimony-thallium, antimony-lead and antimony-tin. The specimens in the form of small cylindrical rods were made from the purest metals obtainable and were melted either in a vacuum or in an atmosphere of nitrogen. The difference in weight in and outside a magnetic field was determined by means of a Sartorius balance, which under favorable conditions gave the weight to one millionth of a gram. The maximum error did not exceed one percent. Curves showing the relation between susceptibility and concentration indicate the formation of the inter-metallic compound Sb-Cd in the cadmium-antimony series, and Sn-Tl in the tin-thallium series. With the addition of thallium to antimony the diamagnetic susceptibility passes through a minimum when the concentration of antimony is about eighteen percent. The lead antimony series shows a similar minimum at fifty percent. The susceptibility of the zinc-cadmium series indicates that zinc is slightly soluble in cadmium, and cadmium slightly soluble in zinc, and the remainder of this series of alloys mechanical mixtures.

51. The emission of positive ions from metals. H. B. WAHLIN, *University of Wisconsin.*—The positive ion emission from metals has been investigated by a mass spectrograph method. It has been found that most metals when first heated give off alkaline ions, as has been observed before. In addition, Cr, Mo, W, Ru, Rh, Nb, Ta, when heated to a temperature where vaporiza-

tion becomes appreciable, give off ions which are singly charged atoms of the electrode material itself. No indications of doubly charged atoms were obtained. Cu, Ag, Au, Zn, Mn, V, Fe, Co, Ni, Pd, Os, Ir, Pt, U, Th, Sb give only alkaline ions. Mn is doubtful. The work is being extended to temperatures above the melting point.

52. Residual ionization in air at new high pressures and its relation to the cosmic penetrating radiation. JAMES W. BROXON, *University of Colorado.*—Residual ionization measurements in air at pressures up to 170 atmospheres were made at 5400 ft. altitude in a spherical chamber of 11-23/32 in. diameter with lead and water shields. Values as low as 1.47 ions/c.c. sec. at 0.83 atmosphere were observed. At pressures above 140 atmospheres ionization-pressure curves obtained with the chamber shielded were parallel to the pressure axis, slopes in this region certainly not exceeding 0.02 ion/cc sec. atm. Increased shielding decreased the ionization, showing the existence of a penetrating radiation. Observations with water shields showed this radiation to have its origin above the level of the chamber. The calculated absorption coefficients are 0.0127 cm^{-1} lead, and 0.0010 or 0.0028 cm^{-1} water, the latter two values following respectively from the extreme assumptions that the radiation approached entirely from the vertical direction, or uniformly from all directions above the horizontal. If the ionization is considered to be due entirely to recoil electrons excited in the walls of the chamber, the pressure-ionization relation may be explained; and if the Compton theory is used, the absorption coefficient of the initial penetrating radiation as calculated from the observed range of the recoil electrons is found to be 0.0025 cm^{-1} water.

53. The effect of hydrogen upon the intensities of the spectra of zinc, cadmium and mercury. J. G. BLACK AND W. G. NASH, *University of Kentucky.*—When hydrogen is mixed with zinc vapor in a low voltage arc, some of the zinc lines change their intensities markedly. (Phys. Rev. **34,** 1138, (1929)). Recent experiments with the related elements, cadmium and mercury, show similar changes. Hydrogen increases the number of transitions to the 2^3P_{012} configuration of all three elements and greatly reduces the number of transitions from the 2^3P_1 state by radiation. The configuration energy is approximately 4.7 volts in mercury, 4 volts in zinc, and 3.78 volts in cadmium. Hg′ has more than enough energy to dissociate hydrogen. Zn′ has almost exactly enough, which fact may account for the total absence of the 3075.8 line. Cd′ does not have enough energy and probably loses its total energy to tube walls and electrodes after it has been made metastable by hydrogen impacts. An alternative explanation of the resonance quenchings is that they are due to the formation of metallic hydrides. It appears that the absence of a Raie Ultime does not insure the absence of an element in chemical spectroscopic analysis when hydrogen is present.

54. The ionization of hydrogen by positive ion impacts. MASON E. HUFFORD, *Indiana University.*—Positive ions of K, Na, Li and H have been accelerated between a filament and an earthed nickel cathode in an atmosphere of pure hydrogen. The cathode was surrounded by a second nickel screen and this in turn was enclosed by a similar screen in contact with the walls of the ionization tube. Ions were accelerated by potentials varying from zero to 2000 volts and retarded beyond the cathode by a potential 7.5 volts more than the accelerating potential. Current-accelerating potential curves show that the relation between ionization current and potential with K-ions is about linear. Increases can well be explained by the action of electrons from the cathode. With other ions the increase of current is much greater. With low pressures the increase in current is such as to indicate ionization by positive ions. At higher pressures distinct critical potentials are shown at voltages about 200 volts below that at which an arc is established.

55. On the fraction of current carried by electrons at the cathode of a mercury arc. K. T. COMPTON, *Massachusetts Institute of Technology.*—Ever since Schottky first pointed out that studies of heat balance afford a possibility of estimating what fraction of the current at arc cathodes is carried by escaping electrons, attempts have been made to do this in the hope of thereby testing theories of the arc. Such work has heretofore indicated that not much more than half this current is carried by electrons,—a conclusion which is difficult to reconcile with

any electron emission theory of the arc cathode because of the impossibility of accounting for a number of positive ions produced by an approximately equal number of electrons which had fallen through a cathode drop amounting to not more than one minimum ionizing potential. Revised estimates are now based on measurements of cathode drop and new considerations involving accommodation coefficients and the destination of electronic energy near the cathode. The conclusion is now reached that between 80% and 100% of the current of the cathode is carried by electrons. Thus it can no longer be said that arc theories based on electron emission from the cathode are disproved by measurements of heat balance.

56. Study of the afterglow in mercury vapor. HAROLD W. WEBB AND DAVID SINCLAIR, *Columbia University.*—The intensity of the afterglow in mercury vapor was studied in a side tube leading from a mercury arc as a function of vapor pressure, concentrations of ions and electrons and electron temperature. The intensity was found to vary roughly as the fourth power of the vapor pressure. Except at very low concentrations it was closely proportional to the first power of the electron concentration. With vapor pressure and concentration held constant, the intensity decreased very rapidly with increase in electron temperature, changing by a factor of 2500 as the temperature increased from 1300° to 5600°K. This change is too large to be explained by the theory of the simple recombination process. The results are well expressed in the form, that the intensity varies directly as the square of the total number of electrons and inversely as the number of electrons having energies greater than 1.2 volt. This suggests that we have a recombination process producing the afterglow, which takes place in two stages of which the second is responsible for the emission of the series lines, and that the effect of the fast electrons is to reionize from the first stage.

57. Problems in the design of a tube to withstand millions of volts. WILLARD H. BENNETT, *California Institute of Technology.*—It appears improbable that further increases in potential which can be produced in high voltage tubes can be hoped for until the mechanisms, themselves, of the causes of puncture have been carefully studied. A study of corona discharge over glass led to the conclusion that for further increases of potential, the potential must be generated in vacuum, and that the field must be roughly normal to the glass wall of the tube. The greatest difficulty in obtaining higher potentials in tubes is due to auto-electronic emission from electrode surfaces. A study of emission from unconditioned metal surfaces of radii of curvature large compared to the distance between the surfaces showed that loose microscopic particles adhering to the cathode can give emission indistinguishable from the emission following the usual breakdown. The metal used as anode was found to determine largely or entirely the field-current characteristics.

58. Experiments with high-voltage tubes. M. A. TUVE, L. R. HAFSTAD, AND O. DAHL, *Department of Terrestrial Magnetism, Carnegie Institution of Washington.*—Measurements have been obtained on the artificial β and γ-rays produced by the high-voltage cascade-tubes and Tesla coils previously described in the Physical Review. The $H\rho$ values of the fastest β-rays, measured by their deflection in a calibrated magnetic field, correspond in voltage-equivalents, using the standard β-ray tables, to the peak voltages applied to the tubes, measured as before by the capacity-potentiometer method. Using a Geiger-Müller tube-counter shielded by six inches of lead, the relative γ-ray intensities from the tubes have been measured through 1, 2, and 3 inches of lead. With the tube operating at about 1,300 kilovolts, the absorption coefficient after filtering through 1 inch of lead is the same (0.47) as that for the γ-rays from radium in equilibrium measured under the same conditions with the same instrument. These β and γ-ray measurements incidentally constitute a verification also of previous voltage-measurements. "Heat working" of the Pyrex, as previously described, has removed the voltage-limitation to such an extent that tubes have operated satisfactorily up to approximately 2,000 kilovolts, this limit (above ground) being set by corona or sparkover to the grounded oil-tank. Experiments are in progress on high-speed protons.

59. Multiplet separations and Zeeman effects. J. B. GREEN, *Ohio State University.*—The methods developed by Houston and Goudsmit are applied to the spectra of tin, lead, and antimony. Using the spectroscopic values of the multiplet separations it has been possible to

determine the g-values for the configuration p^2 of Sn I and Pb I, and for the configuration ^3P+s of Sb, in very satisfactory agreement with the experimental values of Green and Loring, and Back for these elements. Further agreement is found in the case of the ^3P and ^1P of Sn III. The multiplet separations and g-values calculated on Houston's theory adequately explain the anomalies found by Green and Loring in this spectrum.

60. Photometric study of the appearance of spectral lines in a condensed spark. H. V. KNORR, *Antioch College.*—The time interval between the appearance of spectral lines in a condensed spark has been studied by means of a Kerr cell used as an electro-optical shutter. Since there appears to be some question about the meaning of the time intervals measured in this way, photometric observations have been made on the rate of increase in the intensities of such lines. From the rate of increase of the intensity for a particular line, it is possible to find by extrapolation the time at which the intensity is zero, that is, the time of its first appearance. The results obtained by this method are compared with the results obtained by the visual method. Observations were made on the arc lines $2^3P_{012}-2^3S_1$ of zinc and for five air lines appearing in the zinc spark. These three zinc lines appear at nearly the same time. The five air lines also appear at nearly the same time but definitely at a time earlier than the zinc lines. These results are not in agreement with the results obtained by the visual method. The explanation of this discrepancy may be found in the failure of the visual method to take proper account of the threshold of visibility. These results indicate that neither of these methods give data on the life time of the zinc atoms in the excited state but only data on the characteristics of the spark discharge.

61. Spectra emitted in the initial stages of condensed discharges. J. W. BEAMS, *University of Virginia.*—Certain improvements in the Kerr cell method (Phys. Rev. **24,** 35, (1930)), (Program O.S.A. Oct. 31, 1930) have made it possible to study the times of appearance of spectrum lines in condensed discharges as a function of pressure of the gas. In mercury vapor $5461(2^3P_1-2^3S)$ was followed very closely (within less than the limit of precision at pressures above 10 cm) by $4358(2^3P_2-2^3S)$ while $5791(2^1P-3^1D)$ appeared somewhat later. As the vapor pressure of the mercury was increased the time between the appearance of 5461 and 5791 decreased. In a discharge in air 5001 N II $(1^3D'_{1,2}-1^3F'_{2,3})$ appeared first. As the pressure was lowered from one atmosphere the time between the appearance of 5001 and 4631, 4643 N II $(1^3P_2'-2^3P_{2,1})$ was decreased while a slight increase was noted in the time between the appearance of 5001 and the group 5680, 5676, 5667, N II $(1^3P'_{2,0,1}-1^3D'_{3,1,2})$. In a mixture of equal amounts of air and helium the time between the appearance of 5001 N II and 5876 (2^3P-3^3D) increased with lowering of pressure. The results probably indicate that some of the above levels are excited in part at least by secondary processes.

62. The sixth spectrum of arsenic. D. BORG, *Upsala University,* AND J. E. MACK, *University of Wisconsin.*—The lines of the transition $3d^94s\leftarrow 3d^94p$ have been indentified in As VI. In all respects the spectrum agrees with the expectations from extrapolation of the sequence Ni I–Ge V, unlike the As VI classification proposed by P. Pattabhiramiah and A. S. Rao (Zeits. f. Physik **53,** 587, 1929), in which those authors point out anomalies.

63. Heterochromatic photographic photometry in the Schumann region. GEORGE R. HARRISON AND PHILIP A. LEIGHTON, *Massachusetts Institute of Technology and Stanford University.*—The spectral energy responses of several of the fluorescent materials ordinarily used for coating photographic emulsions when used in vacuum spectroscopy have been investigated in the ultraviolet between 4000 and 2300A, and in certain easily reproducible cases the number of fluorescent quanta has been found strictly proportional to the number of incident quanta throughout this range. This fact, taken with the uniformity of contrast previously found under similar conditions (Jour. Opt. Soc. America **20,** p. 313, 1930) appears to furnish a general method of photographic photometry which can be used throughout the extreme ultraviolet, where the sensitivity of most spectral apparatus is too low to permit the use of thermopiles for plate standardization. The method is now being checked directly with fluorite apparatus in the Schumann region, and is being applied in a 21 ft. vacuum spectrograph to the determination of electronic transition probabilities in multiply ionized atoms of the first long period.

64. Intermittent exposure in photographic spectrophotometry over wide intensity ranges. BRIAN O'BRIEN AND E. DICKERMAN O'BRIEN, *Institute of Optics, University of Rochester, N. Y.* —Previous work on the compensation of reciprocity failure in photographic spectrophotometry by intermittency failure imposed on the light beam of higher intensity by interrupted exposure (Phys. Rev. **33,** p. 640 (1929)) has been extended using sector discs with aperture ratio as low as 1/1200, using a mercury arc as source mounted on a carriage with range of movement of 50 meters for varying intensity. Emission of the arc was held constant within ½% (measured radiometrically) by controlled ventilation and electrical input. Errors in measurement of sector apertures and exposure timing were less than ½%. Densities were measured with a thermoelectric microdensitometer. For intensities in ratio 1200:1 and sector disc opening 1/1200 running 28 flashes per sec., and comparing adjacent areas, the difference in density produced by continuous low intensity and interrupted high intensity (for It = const) on Eastman Process plates developed to high gamma was less than 0.01 for all densities from threshold to 1.0 for all wavelengths from 4000A to 2300A for intensities from approximately optimal to 10^{-4} this value. For $\lambda < 2800$A correction was made for atmospheric absorption as measured by Dawson, Granath, & Hulburt (Phys. Rev. **34,** p. 136 (1929)). Reciprocity and intermittency failure separately determined by continuous exposure of same total energy to the higher intensity were as great as 0.20 density units for intensity ratio 10^3.

65. Band spectrum of sulphur. PAUL HUBER, *Ohio State University.*—The band spectrum of S_2 has been investigated in both emission and absorption. An under-water spark was used as a source for the light absorbed by the vapor in a heated tube, while Geissler tubes were used for the emission spectra. The effect of predissociation is especially evident in emission, the $n' \rightarrow 0$ progression suddenly breaking off after the 8-0 band, (λ2828), as reported by Von Iddekinge. The heat of dissociation of normal S_2 is therefore reduced to less than 4.39 volts, as compared with 4.9 volts given by the International Critical Tables. No improvement could be made in the accuracy of the heat of dissociation of excited S_2, because of the extreme irregularities in intensity in emission. Five emission bands lying between λ2828 and λ2980 have been photographed at high dispersion using the second order of a 21-foot grating. The fine structure analysis of these bands is now in progress.

66. Distribution of intensity within the β and γ band systems of nitric oxide. OLIVER R. WULF AND ERNEST J. JONES, *Bureau of Chemistry and Soils, Washington, D. C.*—Variations in the distribution of intensity within the β and γ bands of nitric oxide have been observed when the products from an oxygen discharge tube are allowed to interact with the products from an active nitrogen tube. In this connection attention is called to an abnormal excitation of the γ bands of nitric oxide as they are emitted from an ordinary high current atmospheric pressure arc. The character of the intensity distribution suggests that the excitation arises as a chemiluminescent phenomenon, the energy of excitation being derived from energy made available in reaction. There appears to be evidence for reaction involving metastable nitrogen molecule. If this is the case it illustrates the chemical reactivity in the homogeneous gas phase of one state of the neutral nitrogen molecule. The conditions leading to the alterations in intensity distribution within the band systems mentioned above suggest that the excitation of band spectra is apt to depend on chemiluminescent processes and that the intensity distribution will, therefore, frequently be abnormal.

67. CO bands in the region λ2220 to λ3300. HAROLD P. KNAUSS, *Ohio State University.*—Microphotometer records covering the region from 2200 to 3300A were made of CO band spectra obtained in the electrodeless ring discharge (Knauss and Cotton, Phys. Rev. **36,** 1099, (1930)) and wave-lengths were measured. Unidentified bands at wave-lengths 2925, 3028, 3138, and 3253A were identified as belonging to a new system, corresponding to transitions from $C(^1\Sigma)$ to $a'(^3\Sigma)$. According to values for the known energy levels of the CO molecule quoted by Estey (Phys. Rev. **35,** 309 (1930)), the equation for the new system should be

$$\nu = 34160 - (1173n'' - 9n''^2).$$

Comparison between the observed wave-lengths and those predicted from this formula is made in the following table.

Transition	ν(Calc.)	λ(Calc.)	λ(Obs.)
0–0	34160	2926.5	2925
0–1	32996	3029.8	3028
0–2	31850	3138.8	3138
0–3	30722	3254.1	3253

68. Infrared absorption bands of slightly asymmetric molecules. HAROLD H. NIELSEN, *Ohio State University.*—A set of theoretical curves (as yet unpublished) showing the properties of infrared bands of completely asymmetric molecules have been made by D. M. Dennison. As a complement to these, calculations have been made for molecules of only slight asymmetry. A_x, A_y and A_z have been chosen the three principal moments of inertia of the molecule, where $A_x<A_y<A_z$. Diagrams have been prepared of positions of lines and their respective intensities, determined fron quantum mechanical solutions of asymmetric rotators, where the parameter $\rho=A_x/A_y$ varies by steps of 0.01 within the limits $\rho=0$ and $\rho=0.1$. Direct application of these will be made on the spectrum of Formaldehyde (H_2CO) now under observation.

69. Infrared absorption of formaldehyde vapor. JOHN R. PATTY AND HAROLD H. NIELSEN, *Ohio State University.*—Measurements of Formaldehyde vapor (H_2CO) have been made with a Hilger infrared spectrometer of the Wadsworth type from the visible to 7.0μ. The spectrometer is equipped with a rock salt prism and a Coblentz thermopile, and is used in conjunction with a Moll thermal relay and a Leeds and Northrup high sensitivity moving coil galvanometer. The bands reported by Salant and West have been confirmed and in addition a band of relatively strong intensity was found at 4.7μ and another faint band at 2.3μ. The bands listed in order of their intensities are, 4.7μ, 3.38μ, 1.8μ, 1.4μ, 2.3μ, and 1.25μ. Another faint maximum was found at 1.9μ, but it is believed that this may be a part of the 1.8μ band reported by Salant and West. The band at 3.38μ has been resolved into fine line structure by the aid of a prism-echelette grating spectrometer of the Sleator type. The general characteristics of the band are P, Q and R branches of which the Q branch is relatively weak and a fine line structure of 4.5 cm^{-1}.

70. The spectrum of strontium and barium hydride. W. R. FREDRICKSON AND A. L. WARNTZ, *Syracuse University.*—Bands ascribed to the hydrides of the elements strontium and barium, as obtained by an arc between iron and the element in an atmosphere of hydrogen, lie in the far red end of the spectrum, degrade to the violet, but show no similarity. The strontium bands lie in the region λ7500 to λ6800 with double heads at 7350, 7323 and 7020, 6985, the latter being the more intense. At the far red end of spectrum there is a peculiar intensity distribution, showing no sharp heads and with large open spaces in the fine structure. At high dispersion the 7020 band shows four strong branches, indicating a $^2\Sigma-{}^2\Sigma$ transition. The barium band lies in the region λ6925 to λ6380 and is a $^2\Pi-{}^2\Sigma$ band, showing satellite series which are relatively strong in comparison with the customary P, Q, R series.

71. Comparison of x-ray diffraction intensities in liquid long chain compounds with intensities from computations based on a structure factor. G. W. STEWART AND ROSS D. SPANGLER, *The State University of Iowa.*—Quantitative determination of intensities of x-rays scattered from some liquid long-chain compounds are carried out and the results compared with values obtained from experiments. The determinations are based upon the idea of molecular grouping in liquids. A structure factor of the molecules is used to obtain the intensities. Computations are carried out and comparisons made in the case of eleven normal alcohols and twenty-two octyl alcohols. In the majority of cases, the agreement between experimental and computed values is very good, in a few it is fair, and, in a case or two it is poor. On the whole, the results give convincing evidence in favor of molecular grouping in liquids.

72. Useful accessories for the Siegbahn x-ray vacuum spectrograph. F. K. RICHTMYER, *Cornell University.*—To avoid registration on the photographic plate of minute surface imperfections of the crystal, it has been usual to rotate the crystal, by steps of a few minutes of arc, through a degree or so during an exposure. A device is described, consisting of a telechron

motor and reducing gear, for producing continuous, slow oscillations of the crystal through any desired small angular amplitude. To facilitate rapid identification of spectral lines by comparison with some known line, a special plate holder has been devised by means of which a linear scale may be printed on the photographic plate above the x-ray spectrum. The background due to scattered radiation from the crystal reaching the photographic plate frequently covers up faint lines or makes their measurement difficult. When one is interested in a narrow spectral region the intensity of this background can be materially reduced by placing a wedge a millimeter or two in front of the crystal, somewhat after the manner of the Seemann spectrograph. However, inequality of the x-ray brightness of the focal spot then necessitates that the (spiral) filament should be slowly rotated during exposure.

73. Formation of photographic images on cathodes of alkali metal photoelectric cells. A. R. OLPIN AND G. R. STILWELL, *Bell Telephone Laboratories, Incorporated.*—A method of forming both negative and positive photographic images on the cathodes of potassium and sodium photoelectric cells in vacuum is described. These images are sharp and clear in every detail and can be permanently "fixed" by proper treatment. Among the materials which have been successfully used in treating the exposed surfaces to bring out these images are sulphur vapor, air, oxygen and hydrogen in the ratio of 9 to 1, hydrofluoric acid and bromine. During the time the image is forming, the photoelectric sensitivity of the illuminated portions decreases approximately 30 per cent. After the image is fixed as a permanent record there is little difference between the sensitivity of the cathode area bearing the image and neighboring areas. Photographs of photoelectric cells are shown in which such photographic images are plainly visible.

74. The emission of positive ions from thoriated tungsten. H. B. WAHLIN, *University of Wisconsin* An investigation of the emission of positive ions from thoriated tungsten shows that when heated to a temperature above 2000°C three types of ions are given off: a W ion of mass 184, a second ion of mass 232, and a heavier ion of mass 247 ± 1. This heavy ion may be a mononitride or a monoxide of throium. That it cannot be WO_4 is shown by the fact that it does not disappear when the wire is heated in an atmosphere of hydrogen. Outgassing of the wire at an estimated temperature of 1200°C for 100 hours in a vacuum of 10^{-6} mm does not cause the ion to disappear. Varying the gas pressure in the positive ray chamber from 10^{-4} mm to 10^{-5} mm has no effect on the ion. Prolonged heating at a temperature above 2000°C will cause the 247 ion to decrease with respect to the 232 ion which is assumed to be thorium. Neither the 232 ion nor the 247 ion appeared when unthoriated tungsten or thorium metal were used. An x-ray investigation of the *L* region of samples of thoria ores has so far failed to give any indication that the heavy ion may be of an elementary nature.

75. The dielectric constant of air at high pressures. JAMES W. BROXON, *University of Colorado.*—Measurements of the dielectric constant of dry air at zero frequency were made by a balance method, using a quadrant electrometer as an indicator. The dielectric constant was found to increase linearly with the pressure at the rate of 555×10^{-6} per atmosphere at 18°C., up to 170 atmospheres. The Clausius-Mossotti function passes through a minimum in this region.

76. A lens for use with the concave grating. J. B. GREEN, *Ohio State University.*—When the slit for a concave grating is placed on the circle of half the radius of curvature of the grating the focal plane is found to be on that circle for a vertical astigmatic image. In general, regardless of the position of the slit, the other focus is found to be hyperbola. This method of calculation yields a very simple result useful for the calculation of the lengths of the astigmatic images. For the study of individual lines a sphero-cylindrical lens may be used to correct this astigmatism with a resultant increase in the intensity available, and at the same time, a possibility of markedly increasing the dispersion. A preliminary study of several lines with such a lens has yielded promising results.

77. The anomalous scattering of alpha-rays. MORRIS MUSKAT, *Gulf Research Laboratory, Pittsburgh, Pa.*—The potential field causing the Rutherford-Chadwick anomaly in the alpha-

ray scattering by Mg and Al has been determined by inverting the wave-mechanical expression giving the amplitude of the wave scattered by a spherically symmetrical force as an integral over the potential field of the scattering atom. The anomaly was represented analytically in two different ways. The potential fields for both representations, as derived by the above inversion, are essentially the same, their form depending almost entirely on the single fact that the scattering curves show a marked minimum. In magnitude this potential field never exceeds 10% that of the Coulomb potential. It oscillates in sign and falls off very rapidly with distance from the scattering center, becoming negligible at distances greater than about 5×10^{-13} cm. Its small numerical value and oscillatory character are in marked contrast to the assumptions made heretofore, most of which have been that the potential has the form: $1/\rho^n$, $n\geqq 2$, ρ being the distance from the scattering center. The classical charge equivalent of this potential field is a series of shells of alternating sign of charge, separated by approximately 1.5×10^{-13} cm. Rutherford and Chadwick originally suggested just this type of explanation.

78. Dispersion and refractive index of nitrogen measured as functions of pressure by displacement interferometry. CLARENCE E. BENNETT, *Brown University.*—A method of measuring simultaneously the dispersion and refractive index of a gas is discussed. It is justified on theoretical and experimental grounds and applied to the measurement of these quantities for nitrogen over a seven atmosphere range of pressures at two different temperatures, 30° and 0°C, with a high degree of precision. The results show that the Lorentz-Lorenz relation is followed, and that the dispersion is a linear function of pressure. The value of the Cauchy constant B is found to be 1.95×10^{-16} per cm of mercury pressure. The index of refraction is measured at atmospheric pressure for three wave-lengths, at 0° and 30°C, with a limiting error of one third of one percent in $(\mu-1)$. The dispersion information enables these values to be reduced to infinite wave-length, making possible the determination of the dielectric constant by Maxwell's law. The value 1.000585 so obtained differs by less than two-thirds of one percent in $(\epsilon-1)$ from that measured directly by Zahn. The values of the refractive index for nitrogen under N.T.P. conditions for the wave-lengths 4811A, 5893A, and 6362A, are 1.0002921, 1.0002969, and 1.0002967, respectively.

79. The crystal structure of potassium permanganate. R. C. L. MOONEY, *University of Chicago,* (*Introduced by Henry G. Gale*).—The unit cell size and the space group of potassium permanganate were redetermined, and a structure assigned on the basis of intensity observations from photographic plates. The single crystal oscillation method was used, and the plates interpreted by the method of Bernal. Intensities were evaluated simply by visual estimation. The results indicate the crystal to be based on the simple orthorhombic lattice, having four molecules to the unit cell, and symmetry 2Di-16. The cell size was found to have the dimensions: $a=9.08$A, $b=5.72$A, $c=7.41$A. The values check closely the results of other observers. Symmetry considerations and intensity observations indicated a structure having eleven parameters. By the assumption of a tetrahedral arrangement of oxygen about manganese, and by use of values of ionic radii as given by Goldschmidt, it was possible to determine the parameters. Comparative intensities were calculated for the structure. Hartree's figures for the scattering power at different angles were used. The theoretical values so obtained were found to agree fairly well with observed intensities.

80. Linear time scale for voltage range up to 1000 volts. C. K. STEDMAN, *Paul William Research Fellow, Purdue University,* (*Introduced by K. Lark-Horovitz*).—A circuit generating continuously a voltage wave rising linearly from V_1 to V_2 in time t_2-t_1, and dropping from V_2 to V_1 in time small compared to t_2-t_1, can be connected to the horizontal deflecting plates of an oscillograph to provide a linear time axis. The linear time axis circuit of Beddell and Reich (AIEE Journal **46,** 563 (1927)) is limited to a voltage range as defined by the difference between the ignition and extinction voltages of the G-10 neon lamp of fifteen to twenty volts. It has been found that by substituting the Thyratron FG 17 for the neon lamp, voltage ranges from 60 to 1000 volts or more may be obtained. With the grid of the thyratron connected to its filament negative the range is 60 volts and every additional volt negative on the grid increases the range about 100 volts. Stabilization is easily effected by introducing about a tenth

of a volt into the Thyratron grid circuit from the circuit under investigation. The deflecting plates of even a very low sensitivity oscillograph can be connected directly across the current limiting tube (for which a VT 14 is very satisfactory) with no intervening amplifier. The frequency range is approximately the same as that of a neon lamp. A magnetic field parallel to the axis of the Thyratron improves operation at high frequencies by preventing the discharge from redistributing itself over the electrodes.

81. Apparent fatigue and aging phenomena in the active nitrogen afterglow. CHAS. T. KNIPP AND L. N. SCHEUERMAN, *University of Illinois.*—Last July a 5-liter Pyrex bulb was heat-treated, then primed with dried tank nitrogen to a pressure of 0.2 mm Hg and sealed off. The bulb was energized by a motor-generator high frequency set for intervals of time varying from a flash (about 0.1 sec.) up to 50 or more seconds, and the duration of the afterglow noted. A surprising result was observed. The duration of the afterglow fell off apparently exponentially with *increase* of time of energizing. To further check this point a 12-liter bulb was prepared (last August) and placed in an ice bath. The curve obtained still dropped off, but less abruptly. The maximum duration of the afterglow was about 11 minutes. Just recently, December 22, this same bulb was placed in an ice bath at 1°.5C and again subjected to progressively increasing periods of excitation. The maximum was now about 47 minutes, which, when the excitation was prolonged to 50 sec., was reduced to 26 minutes. The reduction in duration seems to be of the nature of a fatigue. It seems unlikely that it is wholly due to the evolution of water vapor since special precautions were taken to free the bulb and nitrogen of moisture, while the increase in duration on flash seems to be an aging effect favorable to the formation of the active aggregates. A 24-liter bulb after aging 3 months glowed, on flash, for 110 minutes.

82. A preliminary report on a new method of x-ray powder diffraction. T. M. HAHN, *University of Kentucky,* (*Introduced by William S. Webb*).—A preliminary report on a method employing the use of a conical beam of x-rays incident upon powdered crystals arranged in a circular form about the central axis of the cone, normal to the axis. All rays diffracted through an angle θ will be brought together at a common point upon the axis of the cone. A photographic film along this axis receives the record of the diffraction pattern, from which the spacing of the planes of the crystal may be readily determined. Advantages of this method are reduced time of exposure and increased separation of diffraction spots.

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